DEVELOPMENT OF GLAZE WITH ALKALI FREE FRIT

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Technology

In

Ceramic engineering (Industrial Ceramic)

By

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Roll number:-213CR2129

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Under the supervision of

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CERTIFICATE

This is to certify that the thesis entitled, **"DEVELOPMENT OF GLAZE WITH ALKALI FREE FRIT"**, submitted by **Mr. Narayan Dutt Joshi** carried out in **National Institute of Technology, Rourkela**, in partial fulfillment of the requirement for the award of **Master of Technology** Degree in **Ceramic Engineering** is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Prof. Sumit Kumar Pal

Department of Ceramic Engineering

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NARAYAN DUTT JOSHI

ABSTRACT

The term glaze can be defined as a thin layer or coating that is used to coat or seal the ceramic substrate. The glazed ceramic product gives high strength, 0% porosity, good chemical resistant, color, hardness, resistant to chemical attacks, high thermal shock resistant, glossiness, whiteness and decorate. Because of all these characteristic and properties in ceramic glazes which makes glaze useful for the various field such as electrical, chemical, mechanical, tile applications, tableware, sanitary-ware and refractory applications.

In most cases of glazes to tile applications the major problem faced is defect like crazing and peeling due to presences of alkalis ions in the glaze composition which can be cured by developing an alkali-free glass system for glaze composition. For the present work an alkali-free glass system with composition 65% SiO_2, 25% B_2O_3, 6% Al_2O_3, 2%CaO and 2% MgO (in wt %) has been prepared by melt quenching method. The melt quenched glass used as frit for glaze preparations. Two different type of clay bentonite and ball clay have been used in glaze compositions. The amount of bentonite and ball clay has been varied from 1%, 5% and 10%. DSC and TG, Dilatometry, FTIR analysis have been done for the alkali-free glass powder to characterize it. The maturity of glaze had been determined by firing glaze samples at 1050^{o}C, 1100^{o}C, 1150^{o}C, 1200^{o}C, 1250^{o}C and 1300^{o}C. Six glaze compositions have been prepared and applied on the tiles. DSC and TG, Dilatometry, flow test and sieve analysis have been done for all glaze compositions. Vickers hardness, thermal shock resistance and crazing test have been done for glazed samples.

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CHAPTER-I

INTRODUCTION

1.1 INTRODUCTION

A glaze is defined as “a coating or layer which is a glassy substance and it is has been fired to fuse to ceramic product to achieve our desired properties like 0% porosity, color, decorate, strengthen or any other technical application”[1]. A single substance cannot fulfill our requirement that is why coating helps us to get desired properties. On the basis of its firing temperature, composition, raw-material classification of glaze can be done.

The Eastern Mediterranean countries are considered where the first glaze was developed around 3500 BC. The glazes were developed by potters in that time only with propose of coloring the stone only. As time passes the potters did many experiments and discovered making of different colors of glaze and textures and even they learned do multiple layering on the substrate by using different firing cycles at different. That time firing techniques and knowledge of materials processing were poor so glazes were not good in quality. But as the passage of time raw materials with high quality and improved firing techniques and even knowing the role of different additives for different applications promoted the production of different glazes for different applications. Now a day’s glaze is being used in everyday life of human and it is playing a vital role in the field of both traditional and advanced ceramics [2,]. Even if we consider definition that is given by the ASTM for the ceramic glaze is a sealing of ceramic substrate with our desired texture, color, strength, decorate, etc. By glazing of ceramic substrate we can achieve high thermal shock resistance, mechanical strength, chemical resistant, whiteness, 0% porosity, translucency, toughness, hardness and glossiness. Having these all properties glaze can be used in various fields of application such as

electrical, mechanical, sanitary ware, tile application, pottery, refractory, thin film [3] and spark plug.

We can find three components as common in all ceramic glazes [1] which are as following:-

1. **GLASS FOREMER AGENTS (USUALLY SILLICA)**
2. **VISCOSITY AGENT (OFTEN ALUMINA)**
3. **FLUXE (VARIOUS FLUXES)**

RO R_2O Flux, basic, alkaline, or monoxides group	**R_2O_3** amphoteric, neutral, viscosity, or stabilizer group	**RO_2** Glass former, acidic, or dioxide group
Most active flux least to active PbO Lead Na_2O Sodium K_{2O} Potassium LiO Lithium SrO Strontium BaO Barium ZnO Zinc MgO Magnesium CaO Calcium	Al_2O_3 B_2O_3	SiO_2 ZrO_2 SnO_2 TiO_2

Table 1.1- Component present in glaze composition

Here we are developing an alkali free glaze for the tile applications so as per the requirements which are desired for our tiles accordingly we have to choose the glass system for glaze composition.

In the wall or floor tile applications our main concern is to the glaze that is going to be applied on the tiles must be defect free.

Various types of defect are present in glazes when they are applied on ceramic tiles. Defects in ceramic glazes are as following:-

- **Crazing**
- **Crawling**
- **Blistering**
- **Pin holing**
- **Shivering(peeling)**
- **Black Coring**
- **Bloating**
- **Dunting**

The problem that is occurred in a glazed tile like crazing can be cured by using an alkali-free glaze. The defect crazing is happened due to the presence of alkalis in glaze like if we use sodium (Na_2O) as flux in glaze composition it will create a crazing problem. To cure this problem we can replace sodium (Na_2O) by boric acid (B_2O_3) as a fluxing agent in glaze composition.

In the development of alkali-free glaze composition we take an alkali-free glass system which is SiO_2-Al_2O_3-B_2O_3-CaO-MgO and their weight% are 65%, 6%, 25%, 2% and 2% respectively. So from above glass system is clearly visualized that as flux boric acid is used and which is anti-craze for the glaze to tile applications [5].

1.2 OBJECTIVE OF THE CURRENT WORK

Alkali free glaze may provide high thermal shock resistance, good mechanical strength, chemical résistance and high viscosity at high temperature. The following points have been considered as the outline of the current work:

- Formulation of an alkali free glass composition for glaze applications to avoid crazing or peeling type defects.
- After preparation of the alkali free glass powder, the characteristics of glass powder will be carried by FTIR, Dilatometry, and DSC and TG analysis.
- Tile samples preparation to glaze applications and apparent porosity and bulk density measurement of the tile samples. Dilatometry analysis of tile sample to know the thermal behavior.
- A formulation of the glaze composition with varying the amount of the suspending agent such as ball clay and bentonite.
- DSC, TG and Dilatometry analysis for all glaze samples.
- Flow test for all glaze samples.
- Vickers hardness for all glazed samples.
- Determination of the thermal shock resistance for all glazed samples and crazing test of the glazed body.
- Crazing test for glazed samples.

CHAPTER-II

LITERATURE REVIEW

2.1 RAW-MATERIALS USED IN ALKALI FREE GLASS SYSTEM FOR GLAZE COMPOSITIONS

The selections of the raw materials for producing alkali-free glass system completely depend on the application that is desired to us for the final product. The raw materials that were used in making of an alkali-free glass system were as following with their characteristics:

- **Silica (SiO_2)** = It (silica) melted at 1710^oC (3110^oF). Silica is considered as the principle glass former agent for glazes which is often used in glass compositions for making of glazes. Except boron compared to all other oxides in glass compositions for making of glazes silica has low a low expansion and contraction rate. [5]

  Decreasing of the silica will decrease the melting point of the glaze. If we increase the silica will usually (a) will increase the melting point of ceramic glazes.

  (b) Will reduce the fluidity in other words will increase viscosity.

  (c) Increase the resistance of chemical attack.

  (d) Increase the hardness and strength of glazes.

  (e) Reduce expansion.

  In some mat glazes in which decreasing amount of silica will be desired but these glazes will not be as resistant and strong as fritted glazes.

- **Alumina (Al_2O_3) =** It (alumina) is a refractory material that melts at 2050^oC (3722^oF) which is considered as an antiflux. It helps in lowering the expansion and contraction. And help in building the strong chemical links between silica and flux.

Increasing of alumina in glaze composition too much will result in rough surfaces and pinholing. While cooling it also helps to prevent the recrystallization of glass. It gives hardness and durability to the glazes. If we go beyond the certain limits it will promote opacity and mattness [5].

- **Calcium (CaO) =** It is inexpensive and easily available. It is melted at 2572^{o}C (4661.6^{o}F) and this is a high-temperature flux. Below soda and potash it has next highest expansion and contraction rate. It also helps in hardness and durability. When it adds overly then will promote dull surface and does not interfere with colors. It acts as good flux at low and high medium temperatures. High calcium based glaze give the bleaching effect in coloring oxides [5].
- **Magnesia (MgO) =** Magnesia is melted at 2800^{o}C (5072^{o}F). It has also low expansion and contraction rate. As an opacifier can be used in low fire glazes. It increases the surface tension. The high amount of magnesia will result in "magnesia mats" in low and high fired glazes [5].
- **Boric acid (B_2O_3) =** Boric starts melting at 300^{o}C and fusion will start at 700^{o}C. While cooling it does not recrystallize just because of its amorphous nature. In other words even we can say that it acts as silica in the same way. It is also a glass former that helps in melting and it also promotes hardness and strength. Boron makes glazes a little more liable to devitrification [4, 5].

2.2 ROLE OF ALKALI FREE GLASSES SYSTEM IN GLAZE APPLICATIONS

In few literatures it was reported that the term "alkali-free" means that they must be essentially alkali-free it means they contain impurities less.

Alkali free glass systems play a vital role in the glaze applications [6]. Not only for glaze applications but also many applications such as thin film applications, refractory applications, SOFC cell and LTCC applications the alkali-free glass system is being used [7,8]. In the refractory application the alkali-free glass system is being used because low melting phase can be prevented [9]. Thin film transistors, liquid display crystal display screen and plasma assisted liquid crystal display in these applications also the alkali-free glass system is being used and even for dielectric and chemical resistance the alkali-free glass system had been used [10]. Selections or importance of these alkali-free glasses in these applications is due to tis high thermal shock resistance, good chemical durability and high tensile strength [11]. But glazes for tile applications where the role of the alkali-free glass system just because of above-mentioned characteristics of this system is strongly appreciated.

Different type combinations of alkali-free glasses were tried *by Ulrich peuchert et* **al** and which were reported [ref [3], page 7, 8].

On the basis of all different type of perspective for tile application a thin layer coating will be welcomed. Keeping in mind the importance of the alkali-free glasses system for the tile applications and from the above mentioned literature it was decided to use an alkali-free glass system for tile applications to achieve better results in the final product [3].

2.3 ALKALI AND ALKALI FREE GLASS SYSTEM

Either alkali glass system or alkali-free glass system for glaze applications can be studied on the basis of which additives is being added into CMAS (CaO-MgO-Al_2O_3-SiO_2) [12]. The CMAS is a quaternary glass system that is also known as “silceram” [13, 14, 15, and 16]. This is considered as parent glass system for the glaze applications but secondary glass system after adding additives into it gives better results than parent glass system for glazes to tiles applications.

If we add Li2O as additives for CMAS glass system as Li_2O-CaO-MgO-Al_2O_3-SiO_2 then there is a possibility to obtain diopside-based glass ceramic for glaze applications for tiles [17]. However, there are some drawbacks that are considerable not to use alkali glass system for tiles because it does not provide an adequate development of the glaze layer. And for tile applications this drawback is not desired because glazes for tile applications because for tiles surface must be continuous and fault free and along with the glaze must obtain optimum viscosity at maturing temperature to cover biscuits.

To consider as above mentioned glass system if we use it for tiles then it will not effective and economic for tiles. To make our glazes economic and defect free we use boron as an additive in CMAS glass system to obtain an adequate glaze layer for tiles. So the role of additives will decide the final characteristic of the glaze for tiles so adding of additives into CMAS glass system must be done as per desired applications for tiles.

2.4 ROLE OF BORON OXIDE (B_2O_3) IN ALKALI FREE GLASS SYSTEM FOR GLAZE TO TILE APPLICATIONS

To fabricate the ceramic glazes frits are being used just because of their more insoluble nature in water rather than other crystalline raw materials. Frits have both lower and wider melting range. If they are going to be used as a glaze composition ingredient it promotes or favours to obtain a uniform final glaze coating and will help in reducing surface defects [18].

Ceramic glazes for both santitaryware and tableware do not contain borates but borates mainly have been used glazes for wall tiles and floor tiles applications. Materials that give borates are soluble in water so it cannot be used directly to glaze composition. The % amount of the boric oxide in frits depends on the application for which the frit is going to be used. If B_2O_3 added excessively in frit compositions to glaze applications then . As a result pinhole defect will be there. There another defect was observed or reported which is crazing if an adequate amount of boric oxide is not used. Peeling is also a surface defect of glazed tiles which is also decided percentage amount of the boric oxide is used in glass compositions [19].

Elmer et al [19] reported that for B_2O_3 based glass system it is essential that it must be free from the alkalis metals. And he also reported that the addition of B_2O_3 in adequate amount will help in making proper porosity for silica bodies and will also reduce flow temperature of glaze 1000^oC-1250^oC. This addition of B_2O_3 has a small effect upon the thermal expansion coefficient of silica.

2.5 IMPORTANCE OF B_2O_3 IN GLAZES

The Boric oxide has dual use means it acts as a glass former as well as a flux. It considers second largest network former after silicon in glaze compositions. Importance of B_2O_3 in glazes is as follows:

It does not increase thermal expansion even it is a flux

This main reason to use boric oxide in tile glazes. There are other many oxides such as alkalis, alkaline earth etc. which act as flux but they all increase thermal expansion because they are network modifier rather than network former except lead oxide because of its toxic nature the use of lead oxide is restricted.

It improves or promotes glaze appearance

It does not crystallize from the melt and will reduce surface tensions along with it will hinder the crystalline process of another process. These all effects play an important role in productions of the glazes with high glossiness because of low surface tension it gives flat glaze surface. Boric oxide help in promoting gloss but it does not increase the refractive index. For glazes that are colored by dissolved transition metal oxide from them, boron glazes are considered the good base for them.

It improves mechanical and chemical durability

If we use the appropriate amount of the borate in glass compositions for glaze, then it improve both mechanical strengths and also increase the chemical durability. By increasing in adequate manner, borate helps in increasing scratch resistance and mechanical strength. And without boric oxide some glazes are impossible to fabricate.

2.6. ROLE OF SUSPENDING AGENT IN GLAZE COMPOSITIONS

For aqueous slip that requires suspension of the colloidal particles for the coating on the ceramic bodies for that application we require suspending agents in our glaze compositions. Clay is mostly available and commonly used as suspending agent to glaze applications.

Ball clay- generally in white and light colored coating applications the use of ball clay is restricted because of the presence of the impurities in the ball clay. To prevent alteration of colors, it is not used for white coating applications because it can alter the color from 70 to 80 percentages. The addition of ball clay in the glaze compositions up to 12% is desirable.

Bentonite – it is five times stronger than clay in the suspensions and generally used for fully fritted coating applications. Bentonite does not lose its viscosity when it is heated and even does not degrade when bacterial action is there [2].

2.7 PROCESSING TECHNIQUE OF GLAZING ON TILES

The application of the glaze layer or coating on the ceramic tiles can be done by various methods. The various methods to apply coating on the ceramic tiles are depending upon the thickness of layer which is desired for our applications. In some glazes composition, we require an enough thick coating.

Buchanan [20] he reported various type of glass system from which we took glass system for present objective of work and we modify the glass system as per our application and along with explained various methods to apply coating on the ceramic tiles and applications of the coating must be done by the experienced people because the rheology of the glaze slurry should be considered and glaze slip includes suspending agents, binder and hardener. The various methods of the coating on the ceramic substrate are as following:

- **Dip coating**
- **Brushing**
- **Flood coating**
- **Spray coating**
- **Sputtering**
- **Dry pressing**
- **Electrostatic spray coating**

The thickness of the coating that is required for our applications according to the processing technique will be used.

Preheating temperature (^{o}C)	**Coating thickness (mm)**	**Immersion time (seconds)**
100	2	10
100	2.5-3.5	20
100	4-5	30
60	N/A	10
60	1.0	20
60	2.0	30

Table 2.1- Coating vs. immersion time [20].

2.8 VARIOUS DEFECTS

Various defects can be detected if the proper glazing is not done and if appropriate glaze compositions were not selected [1] for tile applications that are as following:

Crazing – Crazing can be considered as the most common defect and which is easiest to cure.

Figure 2.1 – crazing defect

Above fig clearly illustrates the crazing defect. The cause of crazing can be considered as the thermal expansion mismatch of the body and glaze. The ways to cure this defect are:

1. Increase the silica in glaze or body.
2. Decrease the feldspar in glaze or body.
3. Decrease any other materials that contain sodium or potassium.
4. Increase the boron in frit composition.
5. Increase the alumina
6. Increase the lead oxide

Blister - Blister defect is due to the thick coating applications on the tiles. In following it is clearly illustrated.

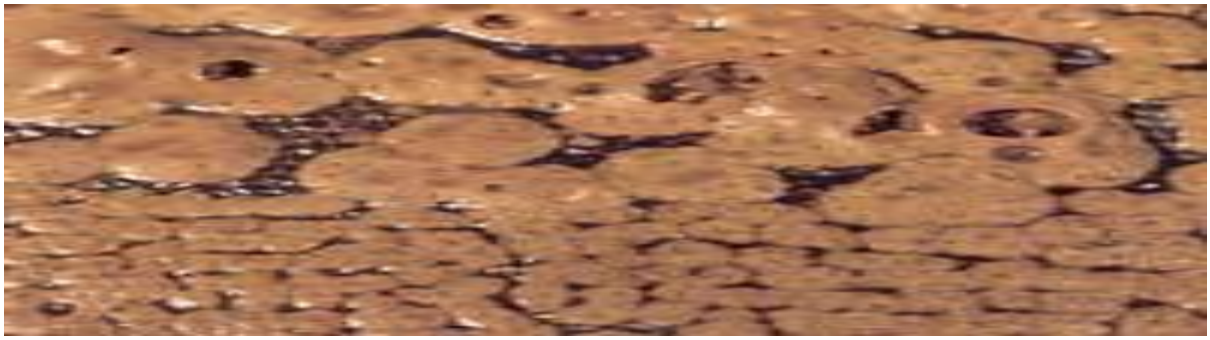


Figure 2.2 – blister defect

Except thick application coating issue it can be due to the incomplete clay preparation. Sometimes this defect can be there due to the over firing or using soluble flux in the glaze composition. There are such fluxes like potassium carbonate, magnesium sulfate, sodium carbonate etc. if they are present in the glaze composition they will create this problem.

Crawling – A high index of the surface tension in melting glaze causes crawling. This is illustrating in following the figure.

Figure 2.3 – crawling defect

In above it is clearly visible the crawling defects. If the bad application of the coating and adhesion of the coating are not good then this defect can be triggered. By addition of the small amount of the gum in the glaze composition this problem or defect can be alleviated. When zinc and magnesium are used excessively this is also issue to create this problem.

2.9 CONCLUSION FROM THE LITERATURE SURVEY

From the above-mentioned literature reviews it is candid that to use of the alkali-free frit for formulating the alkali-free glaze for tile applications is a challenging aspect for the ceramic technologist. With the use of alkali-free glaze to tile applications, various types of defects in tiles can be prevented. Therefore, the alkali-free glass system had been taken for glaze applications.

CHAPTER-III

EXPERIMENTAL WORK

3.1 TILE PREPARATION FOR GLAZE APPLICATION

Here we are developing an alkali-free glaze for tile applications so it is necessary to make tiles for the glaze to apply glaze on tiles for our further testing and characterization. In making of tile sample generally commercially available raw material was used. The raw-materials that were used in tile preparations such as ball clay, china clay, quartz and feldspar these all material can be included in the basic tri-axial compositions.

RAW-MATERIAL	BALL CLAY	CHINA CLAY	QUARTZ	FELDSPAR
WEIGHT%	25	25	25	25

Table 3.1- Tile composition

3.1.1 MIXING AND PRESSING

Above mentioned raw-materials in Table 3.1 were weighed accordingly to composition. Raw-material were weighed and then mixed in a plastic container while mixing water was used as a binder. Water gives a bonding strength to the materials for the compaction. Now the raw-materials are mixed properly with the binder and pressed in uniaxial pressing machine using the hydraulic press and rectangular bars were prepared. During compaction the pressure applied was 6 ton for a dwell time of 120 seconds. Fifty rectangular bars were prepared. During the compaction of powder acetone was used as to clean the die and steric acid as lubricant. And from the following figure the samples of the after compaction is clearly illustrate.

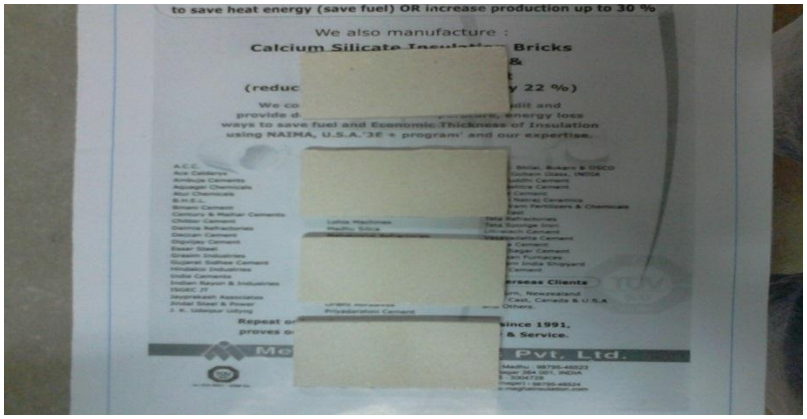


Figure 3.1 - Green tile after compaction

3.1.2. SINTERING OF THE FABRICATED BARS

All tiles were sintered in the electrical furnace at 1250^{o}C and the firing schedule was as the heating rate was 3^{o}C/min and fired up to 1250^{o}C for 120 minutes as soaking time.

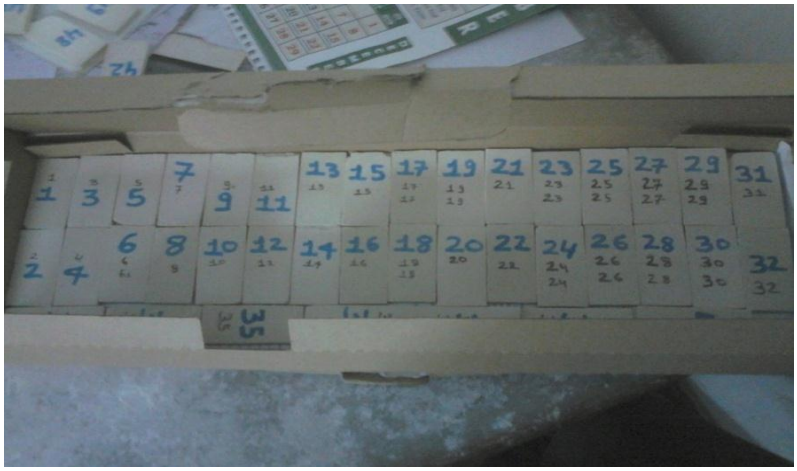


Figure 3.2 – Sintered biscuits

3.1.3. APPARENT POROSITY AND BULK DENSITY

3.1.3. (A) APPARENT POROSITY

The volume fraction of pores or voids are present in the body can help to characterize the apparent porosity. Apparent porosity shows a percentage relation between the volume of the voids space and the total volume of the sample. And it was calculated by the boiling method. Formula was used to calculate the apparent porosity that was

Apparent porosity = (soaked weight –dry weight) / (soaked weight –suspended weight) X100

3.1.3. (B) BULK DENSITY

Bulk density is the ratio between the mass of material of a porous body and its bulk volume. The formula that was used to calculate the bulk density was

Bulk density = (Dry weight /Soaked weight – Suspended weight) X Density of liquid g/cm^3

Here the water was used as a medium to calculate the bulk density and for water its density is 1 gm. /cc.

3.1.4. DILATOMETRY OF GREEN AND SINTERED TILE

For the measurement of the thermal expansion coefficient of both green biscuit and sintered biscuit we used dilatometer. This measurement for thermal expansion coefficient was conducted by dilatometer machine (Netzsch 409C). This examination to determine thermal expansion coefficient was performed at heating rate 10^{o}C/min in oxidizing atmosphere at 1250^{o}C.

Figure 3.3 - left green biscuit and right sintered biscuit

Above figure clearly visualized that biscuit was cut into the rectangular bar with dimension 25mm x 5mm.

3.2 ALKALI FREE GLASS SYSTEM AND RAW-MATERIALS

From the above literature review it had been decided to develop an alkali-free glass system for the glaze making to make tiles free from defects such as crazing and peeling. The alkali-free glass that was decided for the formulation is illustrated in the following table 3.2.

GLASS COMPONENTS	SiO_2	B_2O_3	Al_2O_3	MgO	CaO
WEIGHT%	65	25	6	2	2
RAW MATERIALS	Fused silica	Boric Acid	Alumina	Magnesium Carbonate	Calcium Carbonate

Table 3.2 – Composition of Alkali free glass system

In the above-mentioned compositions silica (SiO_2) is considered as major glass former agent. Alumina (Al_2O_3) is added into this alkali-free glass system as viscosity agent and also as glass forming agent. We add CaO and MgO in the glass system because both oxides help in melting of materials. And remaining raw material is boron trioxide that is added into the glass system as fluxing agent and viscosity agent.

3.2.1. PREPARATION OF GLASS FRITS

From the above table the weight percentage for all raw-materials is mentioned and all raw materials were mixed homogenously as per the mentioned weight percentage in the above table and then filled up in the alumina crucible. At 1550^{o}C homogenously mixed material was melted at heating rate 5^{o}C/min and soaking time was given for 2 hours. After soaking time of the melt material at 1550^{o}C, the quenching of the melt was done into the water for the formulation of the glass frit.

Figure 3.4 – glass frit formulated from the water quenching

3.2.2 FORMULATION OF GLASS POWDER

In a planetary milling machine, the quenched frits from water had been wet-milled in water as medium for 8 hours at 350 rpm, in silicon nitride milling jars. After this processing the wet-milled was dried at 150^{o}C in a dry air oven for 16 hours. Then again the dried powder was grinded for one hour to break agglomeration of the powder at 350 rpm. Then sieve analysis of the grinded glass powder was done and it passed through the sieve of 325 meshes.

The whole processing of the formulation of the glass frits from raw-materials to glass powder can be illustrated in the following flow chart that is the as following in the next page.

RAW MATERIAL

↓

MIXING HOMOGENOUSLY

↓

DECOMPOSITION OF MIXED MATERIAL IN ALUMINA CRUCIBLE AT 900℃

↓

MELTING AT 1550ºC IN ALUMINA CRUCIBLE

↓

WATER QUENCHING

↓

GLASS FRIT

↓

WET MILLING OF GLASS FRITS IN PLANTERARY

↓

MILLED AT 350 rpm FOR 10 HOURS, DONE FOR 3 CYCLES

↓

DRYING AT 150℃ FOR 16 HOURS

↓

GRINDING FOR 1 HOUR AT 350 rpm

↓

GLASS POWDER 120 GRAM

Figure 3.5 - GLASS POWDER

3.2.3. DILATOMETRY OF GLASS POWDER

Dilatometry of the glass powder was done to examine for explaining the thermal behavior and its consistency of the glass powder. Dilatometer (Netzsch 409C) was used to explain it and it was performed at the heating rate 10^{o}C/min in oxidizing atmosphere at 800^{o}C. The prepared sample was in a rectangular bar with dimension 25mm x 5mm.

3.2.4. DIFFERENTIAL SCANNING CALORIMETRY AND TG OF GLASS POWDER

Differential Scanning Calorimetry is the very effective technique to determine the crystallization kinetics of the glass powder. DSC and TG of the glass powder were performed calorimetry(Netzsch STA 409C) at heating rate 10^{o}C/min in oxidizing atmosphere at temperature 800^{o}C. TG analysis tells us the percentage mass loss of the glass powder with temperature.

3.2.5. FTIR ANALYSIS OF GLASS POWDER

To determine bonds present in the alkali-free glass system for this FTIR analysis had been conducted for the alkali-free glass powder. To conduct this analysis the FTIR spectroscopy was used to know bonds present in the alkali-free glass system by using FTIR spectroscopy, "Model: Alpha – E, Company: Bruker". FTIR analysis for the glass powder was conducted in the reflectance mode and plotting of the graph for resulting spectra was done between Reflectance (R) vs. wave number (cm^{-1}) by using origin pro – 8 software.

3.3 ALKALI FREE GLAZE COMPOSITION AND RAW-MATERIALS

In this present experimental work six glaze compositions were prepared which are clearly visualized as per following table:-

COMPONENTS	COMPOSITION-1	COMPOSITION-2	COMPOSITION-3
GLASS POWDER	70 %	70%	70%
BENTONITE	1%	5%	10%
WATER	29%	25%	20%

TABLE-3.3 GLAZE COMPOSITION WITH BENTONITE

Another glaze compositions had been prepared with ball clay that are illustrated in the following table-3.3

COMPONENTS	COMPOSITION-4	COMPOSITION-5	COMPOSITION-6
GLASS POWDER	70%	70%	70%
BALL CLAY	1%	5%	10%
WATER	29%	25%	20%

TABLE-3.4 GLAZE COMPOSITION WITH BALL CLAY

Above mentioned all compositions for glaze was prepared and weighed as per their wight percentage and then mixed homogenously. In the above composition both bentonite and ball clay

plays the role of the suspender and the binder. Water helps in the making slurry of the glaze compositions.

3.3.1. ANALYSIS OF GLAZE MATURITY

Analysis of glaze maturity plays a vital role because its maturity temperature at which it will be matured will decide whether it is suitable for our application or not. In a mortar and pestle a 1 g batch of all six glaze compositions were prepared and mixed well. By using a die punch of 13mm diameter, the mixed powder was compacted into pellets at a pressure of 6 ton and dwell time for 90 seconds on a uniaxial pressing machine. These pellet were fired at 1050^{o}C, 1100 ^{o}C, 1150 ^{o}C, 1200 ^{o}C, 1250 ^{o}C, 1300 ^{o}C and 1350 ^{o}C. After firing is done or firing schedule is completed then examination of these pellets were done if they are having well developed bonding with good glassy phase than it can be concluded as glaze maturity temperature or glaze composition has attained its maturity.

3.3.2. SIEVE ANALYSIS OF GLAZE POWDER

Sieve analysis of glaze powder was done to the sure average particle size range that will be helpful to predict that glaze powder has enough particle size for glaze applications. To conduct this sieve analysis powder must pass through 325 mesh size sieve. If glaze powder passes through this size of sieve mesh then that powder can be used further for coating applications.

3.3.3. FLOW TEST OF GLAZE COMPOSITIONS

Flow test of the glaze is done to examine or determine at which temperature the glaze will flow off or peel off from the ceramic body that is a necessary test for the tile applications which helps to predict what composition will flow at which temperature. To measure or to conduct flow test for all glaze compositions six flow tester were prepared which were made of the same composition that had been taken for the tile compositions. A batch of 5 gram for all glaze

compositions were prepared and shape were given to them like ball. Glaze balls were kept in flow tester and fired at 45¯degree angle.

3.3.3.(A) PREPARATION OF FLOW TESTER

Preparation of the flow testers were done with considering the same composition of tile composition which includes basic triaxial composition such as ball clay, china clay, quartz and feldspar with the same weight percentage which had been taken for the tile composition. The raw materials were mixed and water were added as a binder and mixed powder filled up into the mould to give shape as per following the figure.

Figure 3.6 – Casting of the mixed powder in a rectangular mold

After giving shape to the casted body holes were by made into the casted body to keep glaze balls. Which is as following

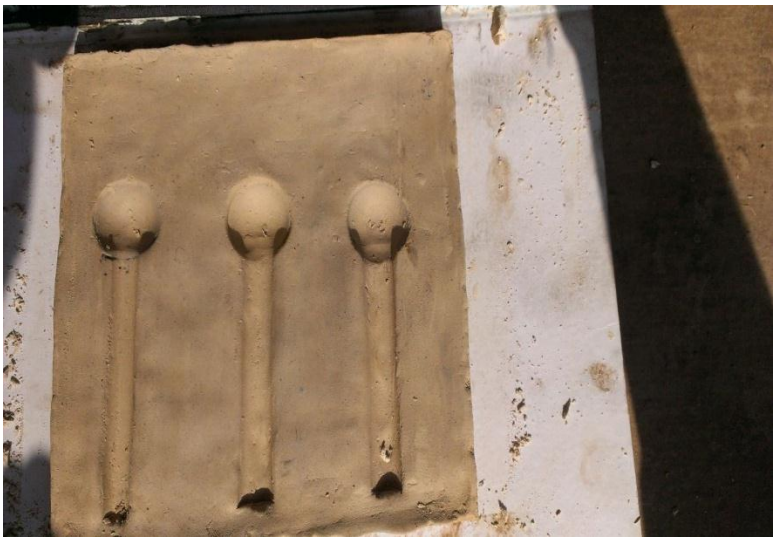


Figure 3.7 - holes made into casted body for keeping sample

After making the holes into the casted body then flow tester were kept in open air drying for 24 hours and then after it was fired at 1250^{o}C with same firing schedule that was followed for tiles.

Now Batch of 5 gram for all glaze compositions were prepared and shape were given to them like a ball. Glaze balls were kept in flow tester and fired at 45^{-}degree angle. The figure for this type of arrangement the main thing or point should be kept in the point that it should be fired at 45-degree angle.

3.3.4. DILATOMETRY OF GLAZE

Dilatometry of all glaze composition were done to examine for explaining the thermal behavior and its consistency between glaze and tile. Dilatometer (Netzsch 409C) was used to explain it and it was performed at the heating rate 10^{o}C/min in oxidizing atmoshpere at 800^{o}C. The prepared sample was in rectangular bar with dimension 25mm x 5mm. In arrangement of dilatometry machine we conduct our test to determine to know the thermal behavior of the glaze powder.

3.3.5. DIFFERENTIAL SCANNING CALORIMETRY AND TG OF GLAZE

Differential Scanning Calorimetry is the very effective technique to determine the crystallization kinetics of glaze powder. DSC and TG of the glass powder were performed calorimetry(Netzsch STA 409C) at heating rate 10^{o}C/min in oxidizing atmosphere at temperature 800^{o}C. TG analysis tells us the percentage mass loss of the glaze with temperature. In DSC machine test of all glaze compositions and glass powder were conducted to know the crystallization kinetics of the glaze powder.

3.3.6. APPLICATION OF GLAZE ON TILES

Brushing method had been used to apply the glaze on the tile and glaze slurry was aqueous enough. Layering or coating of the glaze slurry was coated on the tile samples in such a way that it covered the surface of the tile completely. After application of the glaze on the tiles then all samples were kept for open drying for 24 hours. Then glazed tiles were fired at 1200^{o}C at the soaking time of 2 hours in an electric furnance. In the application of glaze layer or coating it is necessary to uniform coating if uniform coating is not there then there will be a problem in final products after firing. In the following figures, it is illustrating the glaze application on the triaxial samples.

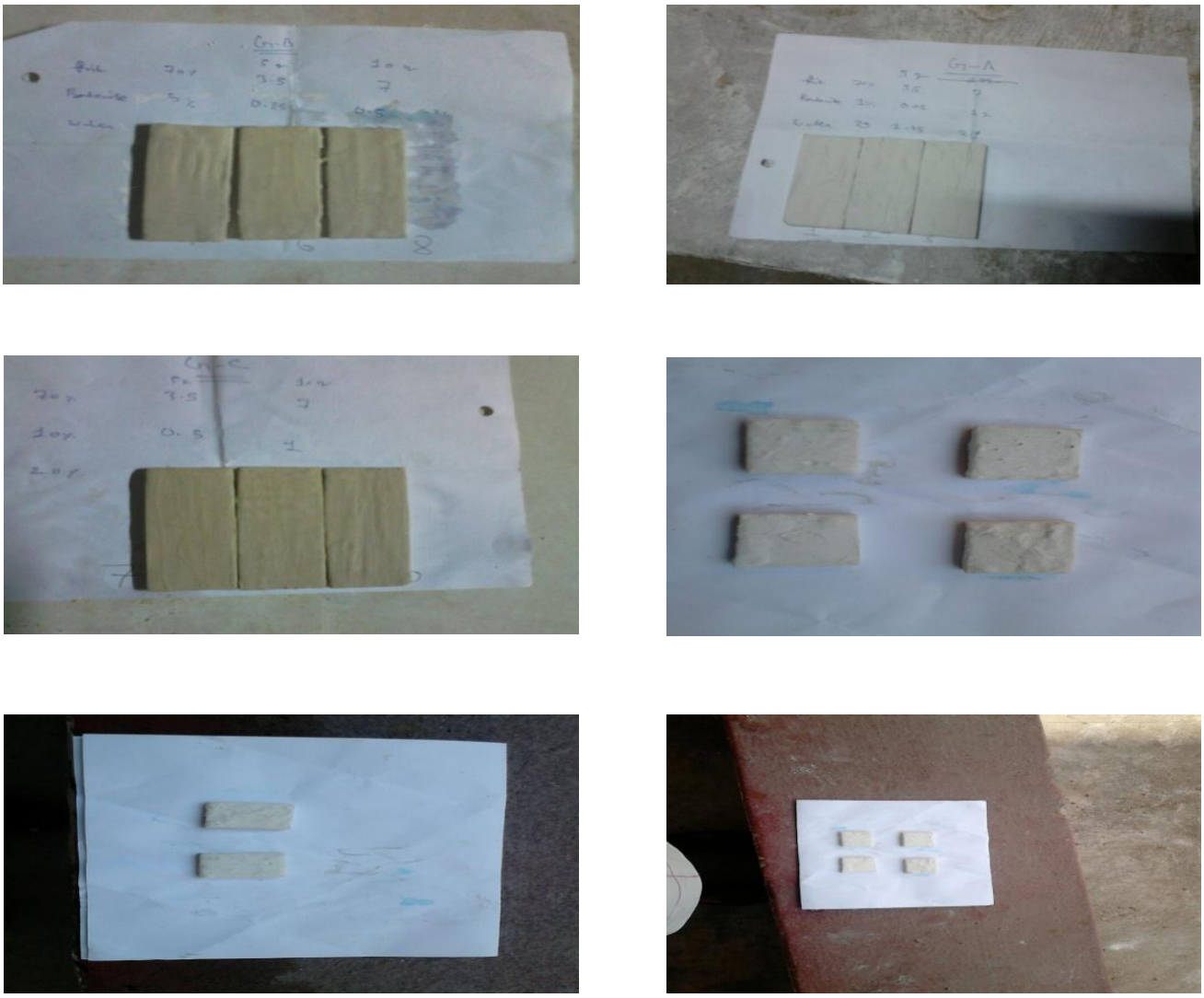


Figure 3.8– Glaze applications on the sintered tile

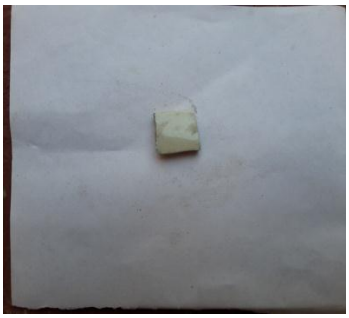
After application of glaze on the tile with all glaze compositions by brushing the glazed sample were fired at 1250^{o}C at a soaking time for 2 hours in an electric furnace. There were various techniques were used to apply the glaze on the tile samples but here brushing gave the desired and uniform coating of glaze.

3.3.7. FIRED SAMPLES AFTER GLAZE APPLICATIONS

(a)

(b)

(c)



(d)

(e)

(f)

Figure 3.9 (a) fired sample of glaze composition-1 (b) fired sample of glaze composition-2(c) fired sample of glaze composition-3 (d) fired sample of glaze composition-4 (e) fired sample of glaze composition-5 (f) fired sample of glaze composition-6

From the above figure, it is illustrating that all applied glaze bodies are fired and after firing all samples gave uniform coating on the tiles.

3.3.9. VICKER HARDNESS OF GLAZED TILE

By Vickers indentation tester-LV 700 machine the hardness of the all glazed samples was determined. Micro indentation was provided to the all glazed samples at a load of 0.5 kgf. The intended area will be in the shape of rhombus because the tip of indention tester is in the shape of a rhombus. By the help of the optical microscope the intended surface can be clearly visualized and along with the length of the diagonals are measured.

Vickers hardness=Hv=(1.8544*p)/d^2

Vickers hardness can be calculated from the above formula where p is applied load and d is the average lenth of daigonals in mm.

3.3.10. THERMAL SHOCK RESISTANCE OF THE GLAZED TILE

Thermal shock resistance was conducted for all glazed sample to determine the resistance of the products or all glazed sample that can withstand at different or rapid firing cycles.

There is no standard method to determine the thermal shock resistance. All glazed sample were fired at 150^o C for one hour and when firing was done then glazed samples were taken out from the oven and immediately sent to water bath, it was done for ten cycles then we observe is there any cracks on the glazed body.

3.3.11. CRAZING TEST OF GLAZED SAMPLES

Crazing test of the glazed samples were conducted in the autoclave machine to know the strength of the glazed samples that at particular pressure and temperature formations of the cracks on the glazed body takes place or not. To conduct this crazing test the glazed samples inserted into the

autoclave machine and programming of the autoclave machine was such as that temperature was fixed at 168^{o}C and when reaching this temperature that time pressure was 200 kpa. And this procedure is done only for one cycle. And there is an increase in temperature by autoclave machine and there is automatically pressure generated in autoclave machine that reached up to 200 kpa at 168^{o}C.

CHAPTER-IV

RESULT AND DISCUSSION

4.1 APPARENT POROSITY AND BULK DENSITY OF THE TILE SAMPLES

4.1.1 APPARENT POROSITY

As per the formula of the apparent porosity of the tiles which follows:

Average apparent porosity = W-D/W-S * 100

Where W = 190.657 gm. (average value)

D = 174.216 gm. (average value)

S = 106.774 gm. (average value)

From the formula of the apparent porosity which discussed earlier in experimental part putting the values of average soak weight (w), average dry weight (d) and average suspended weight (s) of all tile samples.

Average apparent porosity = (190.657-174.216) / (190.657-106.774) x 100

Average apparent porosity for tiles = 19%

Average apparent porosity for all biscuits was obtained 19% which can be considered as good enough porosity for wall tile application and along with 19% apparent porosity also shows that glaze application can be done on the samples.

4.1.2 Bulk Density of tiles

The bulk density of the tiles can be calculated by the following formula that is illustrated earlier in the experimental part.

Bulk density = Dry weight / (soak weight- suspended weight) x density of liquid

Here I did this by boiling method and water as medium and as we know that the density of the water is 1.

We put the value of the average dry weight, average soak weight and average suspended weight in the bulk density formula.

Bulk density = 174.216/ (190.657 – 106.774) x Average bulk density = 174.216/83.883

The average bulk density of tile samples = 2.08 gm. /cm^3

The average bulk density of the tile samples is obtained 2.08 gm. / cm^3 it is an adequate value for the tile samples for glaze application.

4.2 Sieve Analysis of glaze powder

Sieve analysis for all samples of glaze powder were conducted to determine average particle size for this analysis all Samples of glaze powder were passed through the sieve size of 45 micron and all glaze powder samples passed through it and no residual power was left for all glaze samples. It shows that particles of the glaze powder are fine enough for glaze applications and along with by sieve analysis it is also giving confirmation that the size of glaze powder is below the 45 microns.

4.3 Analysis of Glaze Maturity Temperature

Determination of the glaze maturing temperature was done for all samples as per described or mentioned method in the experimental work part. The pellets which were prepared for all samples were fired at 1100^{o}C, 1150^{o}C, 1200^{o}C, 1250^{o}C, 1300^{o}C and 1350^{o}C. After firing was done for all samples then checked visibly to at which temperature the sample attained their substantial glassy phase. Except at 1300^{o}C no glassy phase was observed for remaining temperature. At 1300^{o}C it was observed and found that glaze powder has attained substantial glassy phase and this temperature glaze powder was considered in its optimal state. The temperature above the glaze

Maturity temperature glass frit had started melting so that temperature could not be considered as glaze maturity temperature. So the glaze maturity temperature was fixed at 1300^{o}C.

4.4 FLOW TEST OF ALL GLAZE SAMPLES WITH BENTONITE AS SUSPENDING AGENT

4.4.1 GLAZE FLOW ANALYSIS AT 1050^{o}C

(a) **(b)**

Figure 4.1 (a) before firing at 1050^{o}C (b) after firing at 1050^{o}C

From the above figure it is clearly visualized that when do flow test for all three glaze composition with bentonite at temperature 1050^{o}C there is no flow was observed**.** As we can see in the above figure that for composition – 1 whiteness is good because as we see that increasing of the bentonite percentage whiteness is decreased, which may be due to impurity present in the bentonite.

4.4.2 GLAZE FLOW ANALYSIS AT 1100^{o}C

(a) **(b)**

Figure 4.2 (a) before firing at 1100^{o}C (b) after firing at 1100^{o}C

From the above figure, it is clearly visualized that at temperature 1100^{o}C still there is no flow for the composition – 1 and composition – 3. Only a little flow for glaze composition – 2 was observed at 1100^{o}C**.** But glossiness for all three glaze compositions increased, confirming glassy phase formation. So at this there is no flow was observed except for glaze composition – 2. By this flow analysis at this temperature, we can say that there will be no flow for glaze compositions except glaze compositions -2 for which the a little flow was observed.

4.4.3 GLAZE FLOW ANALYSIS AT 1150^{o}C

(a) **(b)**

Figure 4.3 (a) before firing at 1150^{o}C (b) after firing at 1150^{o}C

From the above figure, it is clearly visualized that there is no flow of the glaze composition of one and little flow was observed for glaze composition two 1150^{o}C**.** From the above analysis, we can say that there will be no flow for even glaze composition – 3.

4.4.4 GLAZE FLOW ANALYSIS AT 1400^{O}C

(a) (b)

Figure 4.4 (a) before firing at 1400^{o}C (b) after firing at 1400^{o}C

From the above figure, it is clearly visualized that there is start of flow for glaze composition – 1 at 1400^{o}C. From the above figure we can see that at 1400^{o}C there is a flow of glaze composition – 2 and this glaze composition – 2 covers almost half of the length of flow tester. For glaze composition – 3 still there is no flow was observed at 1400^{o}C. The sample 3 was having 10 weight % bentonite that essentially increase the amount of alumina and silica in the glaze composition. As these two oxides offer high viscosity at high temperature therefore, there is almost no flow has been observed, the glassy phase formation is due to the presence of high amount of boron in frit composition. Boron generally creates liquid phase at a lower temperature but the presence of no alkali and presence of high amount of alumina and silica prevents the flow of glaze at high temperature. The essential criteria for good glass formation are attaining high viscosity at melting temperature followed by rapid quenching. Due to high amount of silica and

Alumina, the high value of viscosity was observed at high temperature but on the other hand the flow property was less for all the samples.

4.5 FLOW ANALYSIS OF ALL THREE GLAZE COMPOSITION WITH BALL CLAY AS SUSPENDING AGENT

4.5.1 FLOW ANALYSES AT 1300^{O}C

(a) **(b)**

Figure 4.5 (a) before firing at 1300^{o}C (b) after firing at 1300^{o}C

From the above figure 4.4 it is clearly visualized that at temperature 1300^{o}C for glaze composition four, five and six there is no flow was observed**.** But ball clay as suspending agent it gives good transparency and with improved glossiness for all glaze samples

4.5.2 FLOW ANALYSIS AT 1400^{O}C

(a) **(b)**

Figure 4.6 (a) before firing at 1400^{o}C (b) after firing at 1400^{o}C

From the above figure it is clearly visualized that at 1400^{o}C temperature there is no flow was observed for glaze composition – 6. And the little flow was observed for glaze composition – 4. For glaze composition – 5 there was a little flow was observed even we can say that it covered almost half of the length of the flow tester**.** It can be concluded that using the ball clay as suspending agent gives good transparency and glossiness than bentonite.

4.6 COMPARISON OF FLAW ANALYSIS FOR BALL CLAY BASED GLAZE COMPOSITIONS AND BENTONITE BASED GLAZE COMPOSITIONS AT $1400^{O}C$

(a) **(b)**

Figure 4.7 Comparison of flow test for both suspending agent ball clay and bentonite at **1**$400^{O}C$

From the above figure it is clearly visualized that if we do comparison of flow of all glaze sample varying the amount of the suspending agent such as ball clay and bentonite at $1400^{o}C$ it is illustrate from the above figure the flow behavior of 5% ball clay and 5% bentonite with glass powder is almost same both composition – 2 and composition – 5 covers the half of the length of the flow tester. And there is no flow was observed for 10% ball clay and 10% bentonite at temperature up to 1400^{o} C.

4.7 DILATOMETRY ANALYSIS

4.7.1 DILATOMETRY ANALYSIS OF GREEN BISCUIT

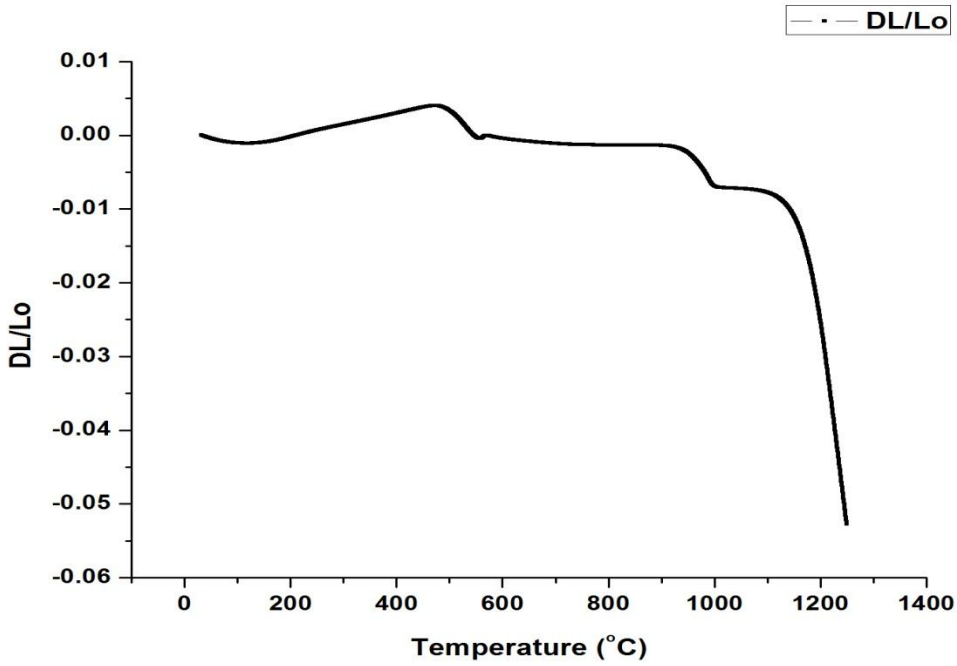


Figure 4.8 Dilatometry analysis of green biscuit at 1250^{o}C**.**

From the above graph at 110^{0}C there is expansion with the removal of absorbed water. From 110^{0}C to 480^{0}C there is a trend of linear expansion. From 490^{0}C to 560^{0}C again there is the trend of linear shrinkage. From 950^{0}C to 1010^{0}C again there is a decrease in dimensions of the body. From 1122^{0}C there is a rapid shrinkage up to 1250^{0}C. There is a contraction from 124^{0}C to 484^{0}C followed by sharp expansion till 562^{0}C. After that there is no change in dimension till 940^{0}C and at this temperature there is again small sharp expansion till 1000^{0}C and this again followed by no change in dimension till 1107^{0}C and at this temperature a very sharp decrease in dimension takes place. The overall contraction was 5% from room temperature to 1250^{0}C. At around 1250oC the liquid phase formation takes place in the sample.

4.7.2 DILATOMETRY ANALYSIS OF SINTERED BISCUIT

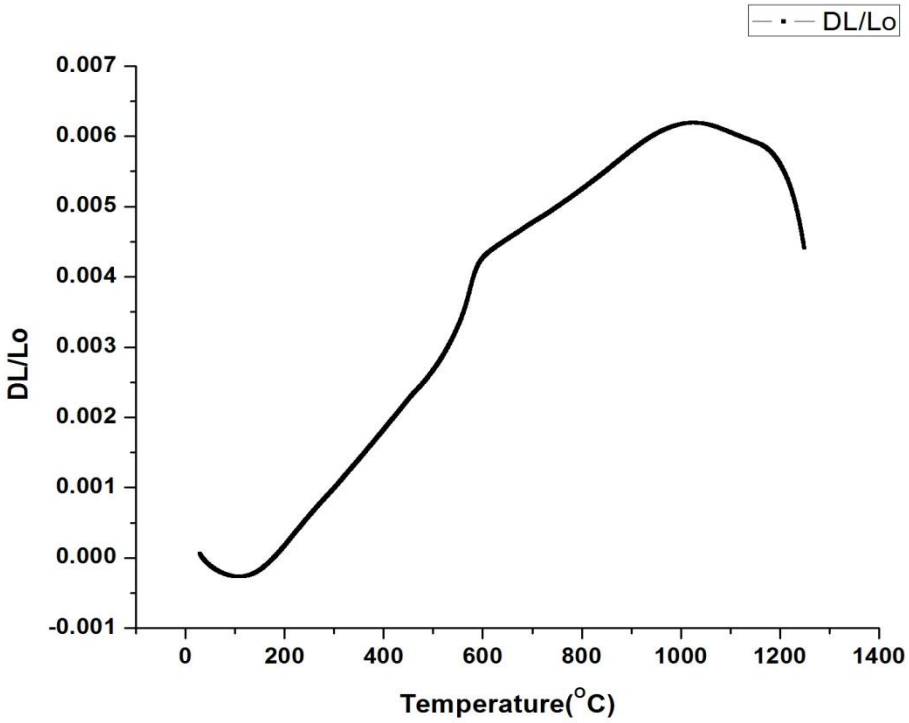


Figure 4.9 Dilatometry analysis of sintered biscuit at 1250^{o}C

At 110^{0}C all absorbed water had been removed from the body. From 110^{0}C to 1050^{0}C there is a rapid expansion. From 1050^{0}C to 1175^{0}C there is shrinkage and after that there is rapid shrinkage up to 1250^{0}C.

4.7.3 COMPARISON DILATOMETRY ANALYSIS OF THE GREEN BISCUIT AND SINTERED BISCUIT

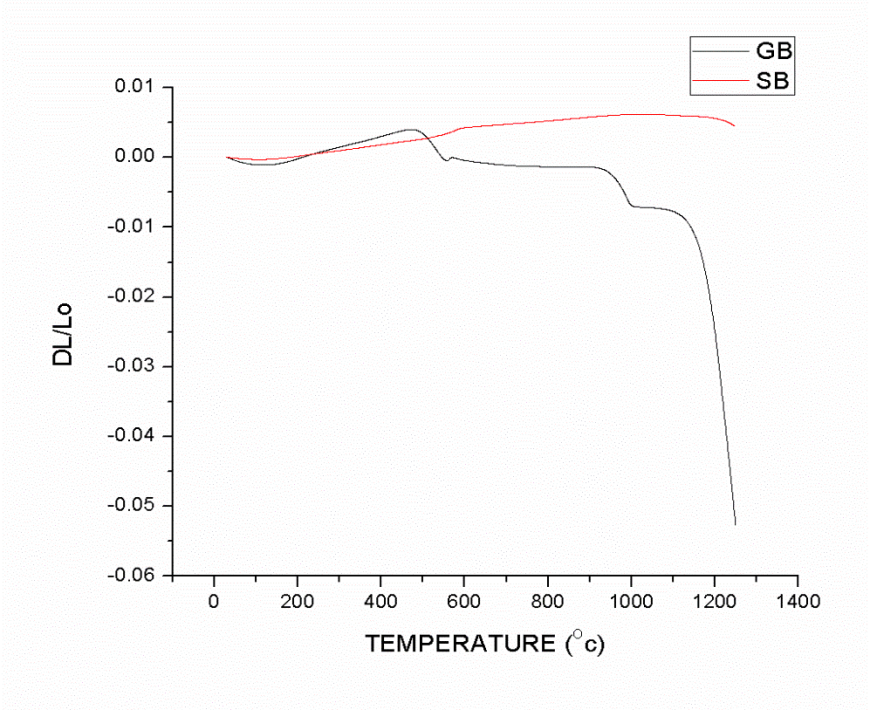


Figure 4.10 comparison dilatometry analysis of green biscuit and sintered biscuit at 1250^{o}C

From the above graph at 110^{0}C there is expansion with the removal of absorbed water. From 110^{0}C to 480^{0}C there is a trend of linear expansion. From 490^{0}C to 560^{0}C again there is the trend of linear shrinkage. From 950^{0}C to 1010^{0}C again there is a decrease in dimensions of the body. From 1122^{0}C there is a rapid shrinkage up to 1250^{0}C. There is a contraction from 124^{0}C to 484^{0}C followed by sharp expansion till 562^{0}C. After that there is no change in dimension till 940^{0}C and at this temperature there is again small sharp expansion till 1000^{0}C and this again followed by no change in dimension till 1107^{0}C and at this temperature a very sharp increase in dimension takes place. The overall contraction was 5% from room temperature to 1250^{0}C. At around 1250oC the liquid phase formation takes place in the sample. And for the sintered tile just it showing little shrinkage it means sintered tiles are good to apply glaze on it.

4.7.4 DILATOMETRY ANALYSIS OF GLASS POWDER

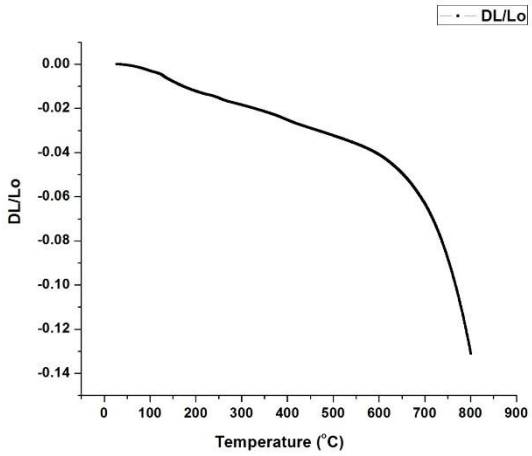


Figure 4.11 – Dilatometry analysis of glass powder at 800^{o}C

As temperature increases, there is shrinkage up to 650^{0}C and after that there is rapid shrinkage was observed up to final temperature. Samples undergo little expansion till 650^{0}C beyond that a sharp increase in dimension of the sample takes place. The shrinkage is 11% up to end for glass powder.

4.7.5 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION - 1

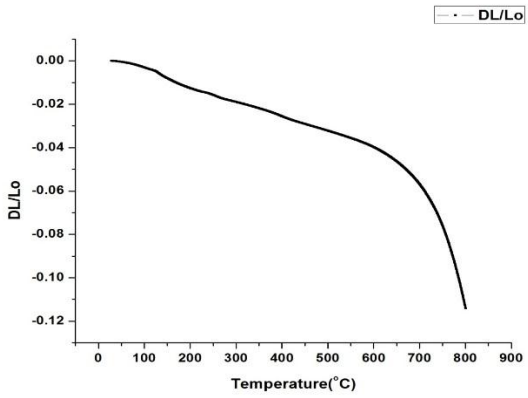


Figure 4.12- Dilatometry analysis of composition - 1 at 800^{o}CAs temperature increases there is shrinkage up to 670^{0}C and after that there is rapid shrinkage was observed up

to final temperature. At 650 ^{o}C there is shrinkage and this region where the liquid phase can be considered. There is around 11.5% shrinkage is observed.

4.7.6 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION -2

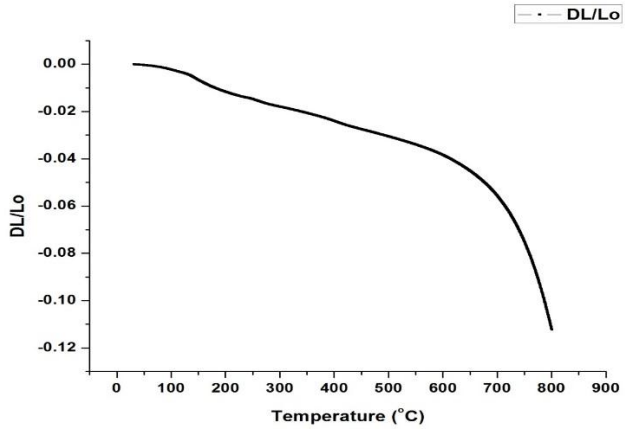


Figure 4.13- Dilatometry analysis of glaze composition – 2 at 800^{o}C

From 135^{0}C to 200^{0}C there is a sharp shrinkage slope is observed. And after that there is the trend of linear shrinkage up to 670^{0}C and after that is a rapid decrease. There is 11% shrinkage for GC-2.

4.7.7 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION - 3

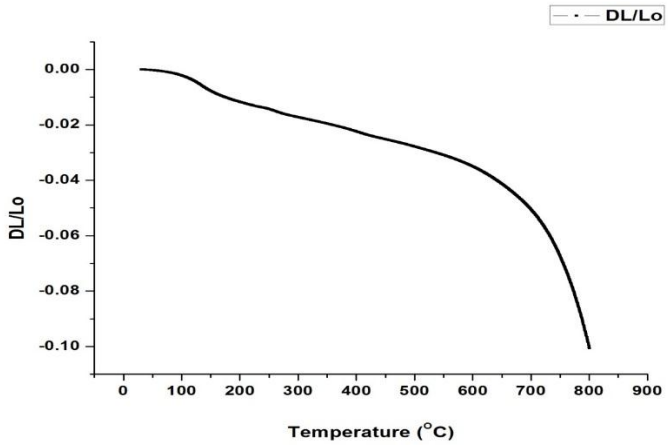


Figure 4.14 Dilatometry analysis for glaze composition – 3 at 800^{o}C

From 130^{0}C to 225^{0}C there is a sharp shrinkage slope is observed. And after that there is the trend of linear shrinkage up to 660^{0}C and after that is a rapid decrease. There is around 9.5% shrinkage.

4.7.8 DILATOMETRY ANALYSIS OF ALL THREE COMPOSITIONS OF BENTONITE WITH GLASS FRIT

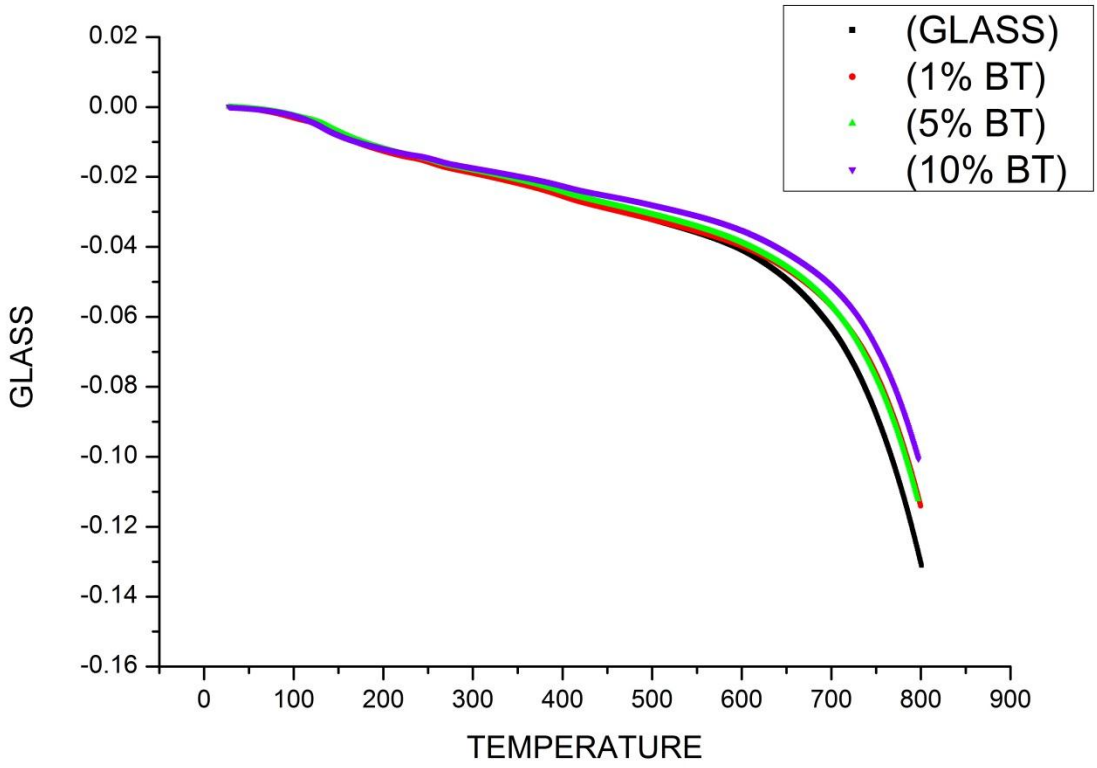


Figure 4.15dilatometry analysis of all three glaze sample of bentonite with glass at 800^{o}C

The above figure shows the dilatometry of four green bars (glass, 1%,5% and 10% BT) from room temperature to 800^{0}C. The heating rate 10^{0}C/minute was maintained for all measurements. An overall shrinkage of 13% occurred for glass sample. For 1% BT and 5% BT samples,

shrinkage were almost same which around 11% is. For 10%BT sample shrinkage was minimum i.e. 9.5%. It can be observed that with an increase in the percentage of BT there was a reduction in shrinkage behavior of around 3.5%. Thus, the addition of BT reduced the shrinkage. This may be due to the increase in silica as well as alumina content in the glaze samples as we increase the bentonite percentage in the glaze composition.

4.7.9 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION – 4

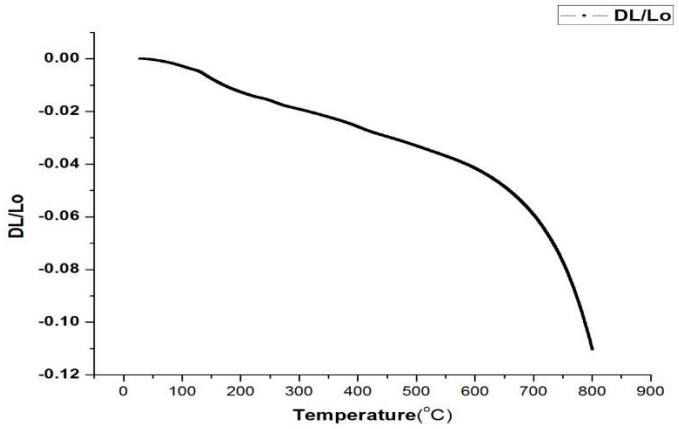


Figure 4.16 Dilatometry analysis of glaze composition – 4 at 800^{o}C

From 130^{0}C to 250^{0}C there is a sharp shrinkage slope is observed. And after that there is the trend of linear shrinkage up to 660^{0}C and after that is a rapid decrease. There is 11.5% shrinkage around.

4.7.10 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION -5

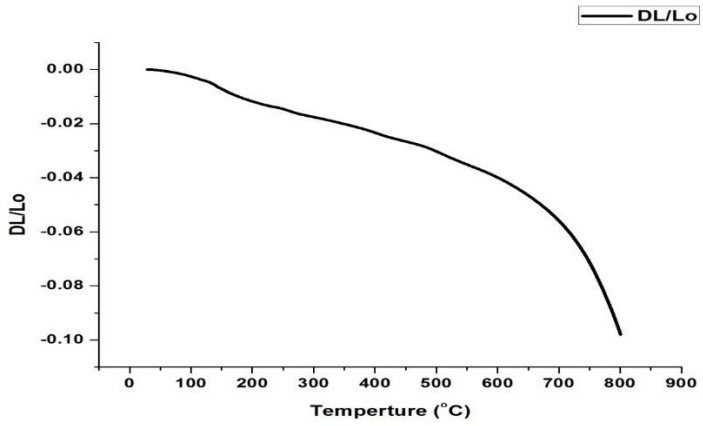


Figure 4.17 Dilatometry analysis of glaze composition – 5 at 800^{o}C

From 130^{0}C to 250^{0}C there is a sharp shrinkage slope is observed. And after that there is the trend of linear shrinkage up to 670^{0}C and after that is a rapid decrease. There is 9.5% shrinkage.

4.7.11 DILATOMETRY ANALYSIS OF GLAZE COMPOSITION -6

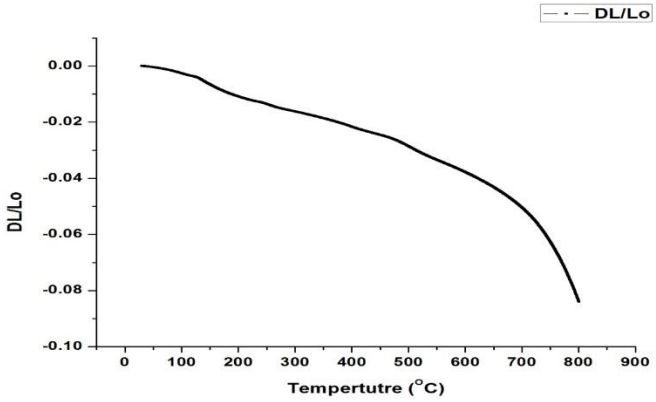


Figure 4.18 Dilatometry analysis for glaze composition – 6 at 800^{o}C

From 130^{0}C to 240^{0}C there is a sharp shrinkage slope is observed. And after that there is the trend of linear shrinkage up to 700^{0}C and after that is a rapid decrease to end. From room temperature to the up to the end temperature which is 800^{o}C at this temperature percentage shrinkage is 8.5%. If we compare from the dilatometry analysis for glaze composition – 3 and

glaze composition -6 it was found or observed that increase the percentage amount of the clay in glass composition there is decrease in the shrinkage of the percent. Along with it was also observed that ball clay lesser the shrinkage than bentonite.

4.7.13 DILATOMETRY ANALYSIS OF ALL GLAZE COMPOSITION OF BALL CLAY WITH GLASS FRIT

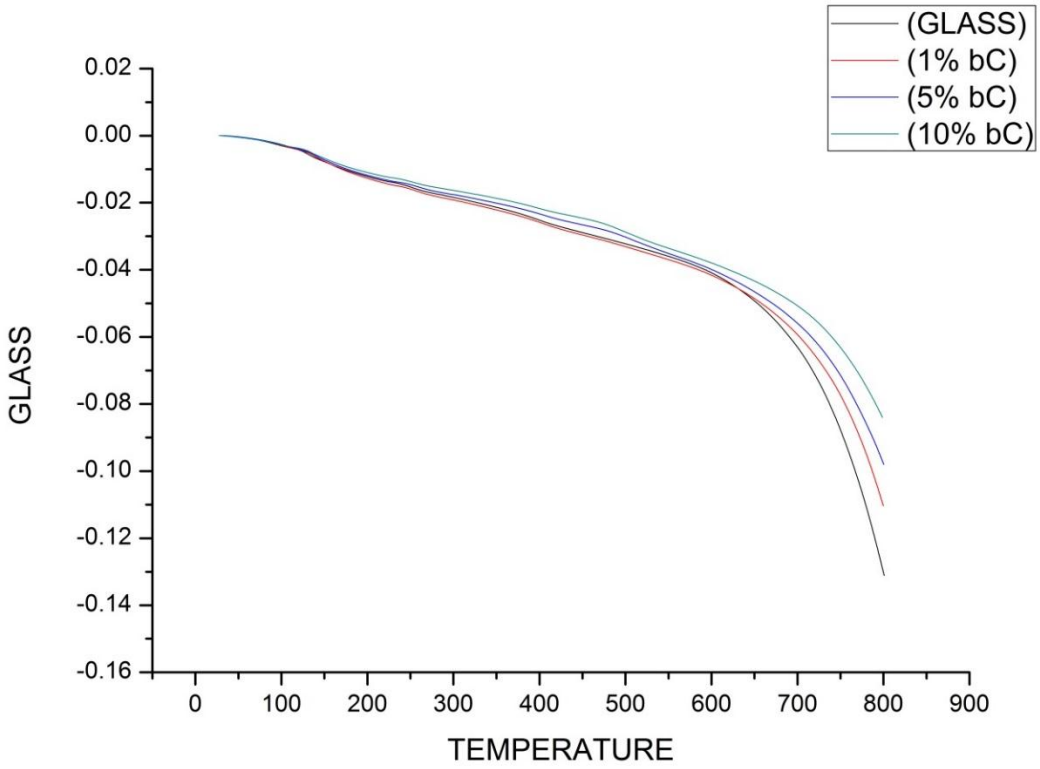


Figure 4.19 dilatometry analysis of all three glaze sample of ball clay with glass

The above figure shows the dilatometry of four green bars (glass, 1%,5% and 10% BC) from room temperature to 800^0C. The heating 10^0C/minute was maintained for all measurements. An overall shrinkage of 12.5% occurred for glass sample. For 1% BC and 5% BC samples, shrinkage was almost same which around 11% is. For 10%BC sample shrinkage was minimum i.e. 8.5%. It can be observed that with increase in the percentage of BC there was a reduction in

thermal shrinkage behavior of around 3.5%. Thus, the addition of BC reduced the shrinkage. This may be due to the increase in silica as well as alumina content in the glaze samples as we increase the ball clay percentage in the glaze composition. From above comparison, it can be observed that ball clay reduce much shrinkage than bentonite.

4.8 DSC AND THERMOGRAVIMETRY ANALYSIS

4.8.1 DSC AND TG ANALYSIS OF GLASS POWDER

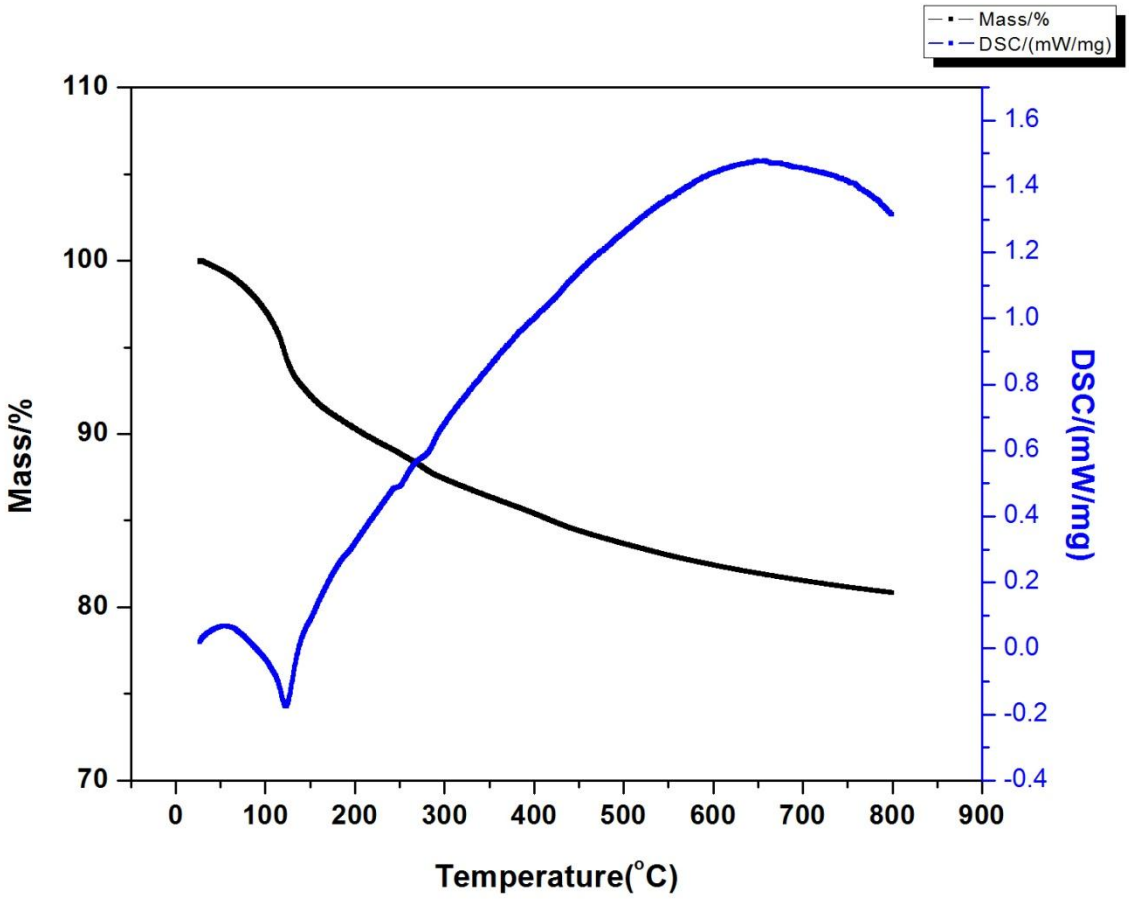


Figure 4.20 DSC and TG analysis of glass powder

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800°C with 17% weight loss. In the first stage the weight loss was 7%

due to the removal of the physically absorbed water and the endothermic peak was shown at 128^{o}C. The second weight loss was around 11%.

4.8.2 DSC AND TG ANALYSIS GLAZE COMPOSITION -1

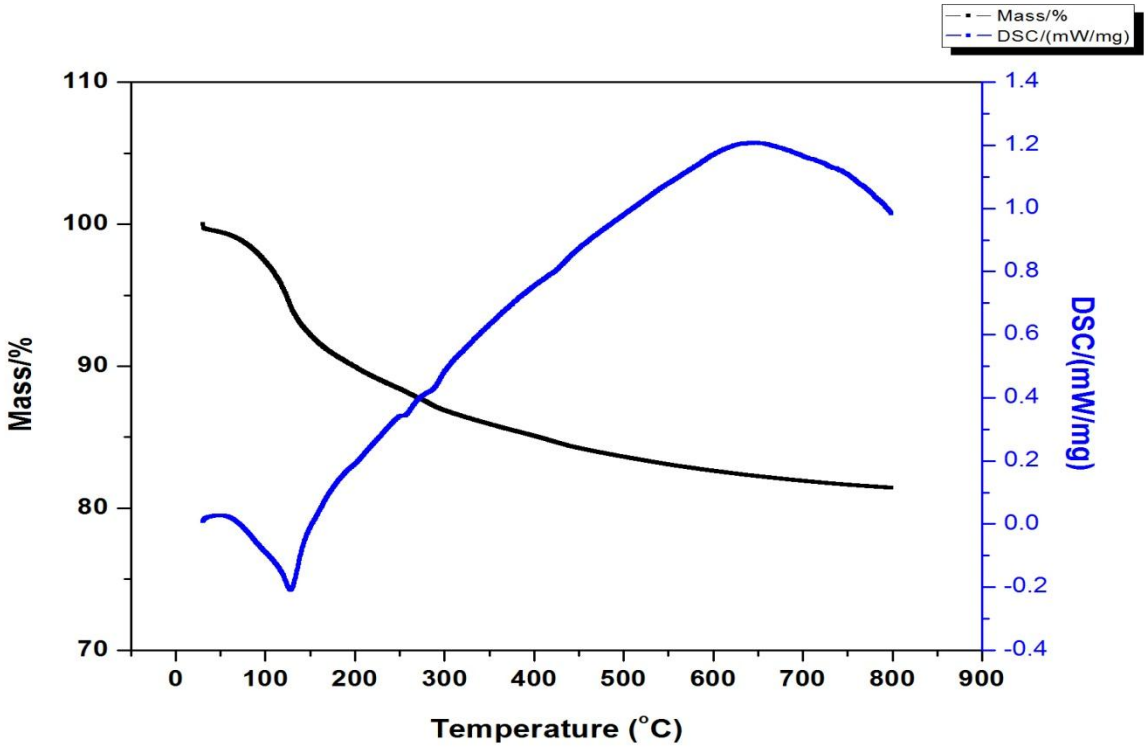


Figure 4.21 DSC and TG of glaze composition – 1 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 15% weight loss. In the first stage the weight loss was 8% due to the removal of the absorbed water and the endothermic peak was shown at 140^{o}C. The second weight loss was around 10%.

4.8.3 DSC AND TG ANALYSIS OF GLAZE COMPOSITION -2

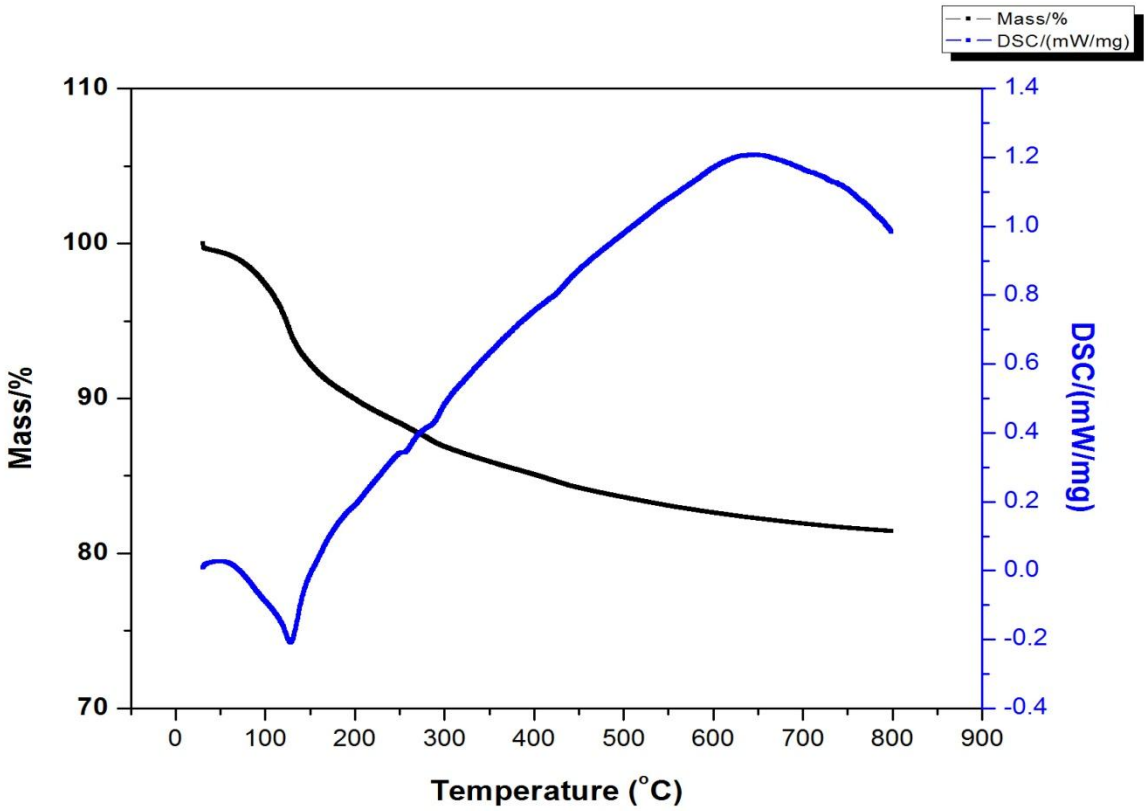


Figure 4.22 DSC and TG of glaze composition – 2 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 18% weight loss. In the first stage the weight loss was 5% due to the removal of the absorbed water and the endothermic peak was shown at 130^{o}C. The second weight loss was around 13%.

4.8.4 DSC AND TG ANALYSIS OF COMPOSITION -3

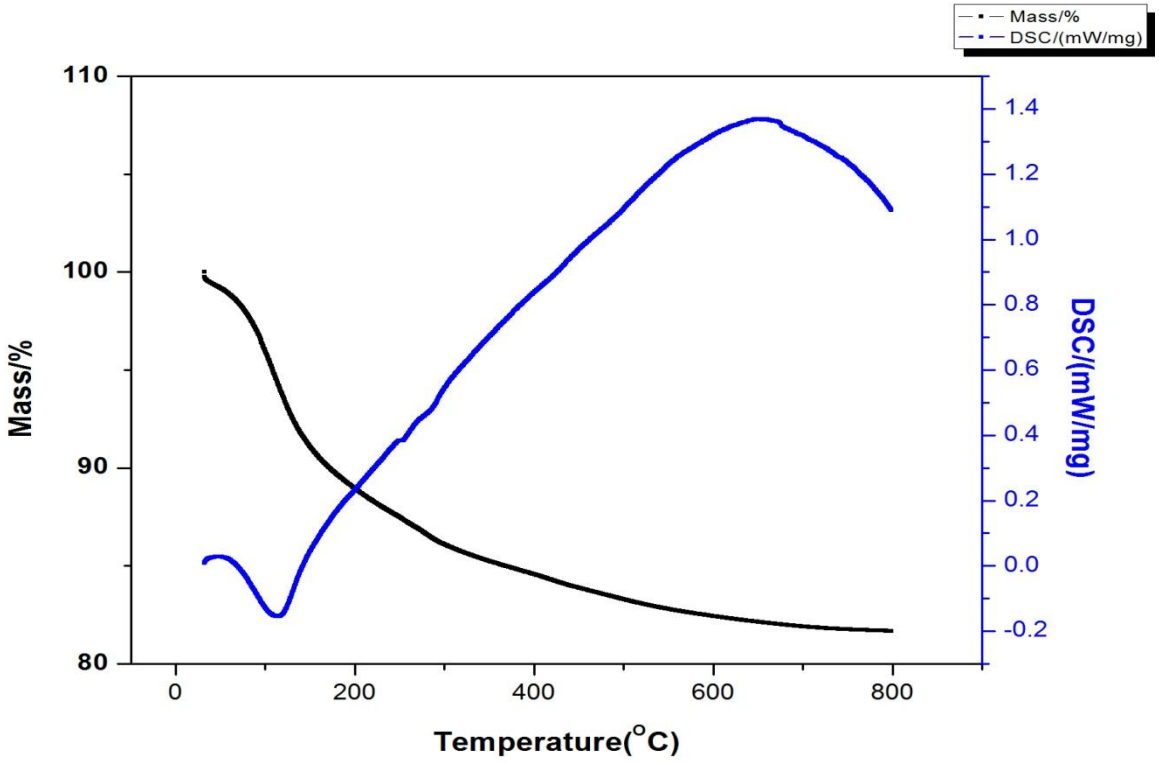


Figure 4.23 DSC and TG of glaze composition – 3 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 18% weight loss. In the first stage the weight loss was 7% due to the removal of the absorbed water and the endothermic peak was shown at 130^{o}C. The second weight loss was around 9%.

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4.8.5 DSC AND TG ANALYSIS OF GLAZE COMPOSITION –4

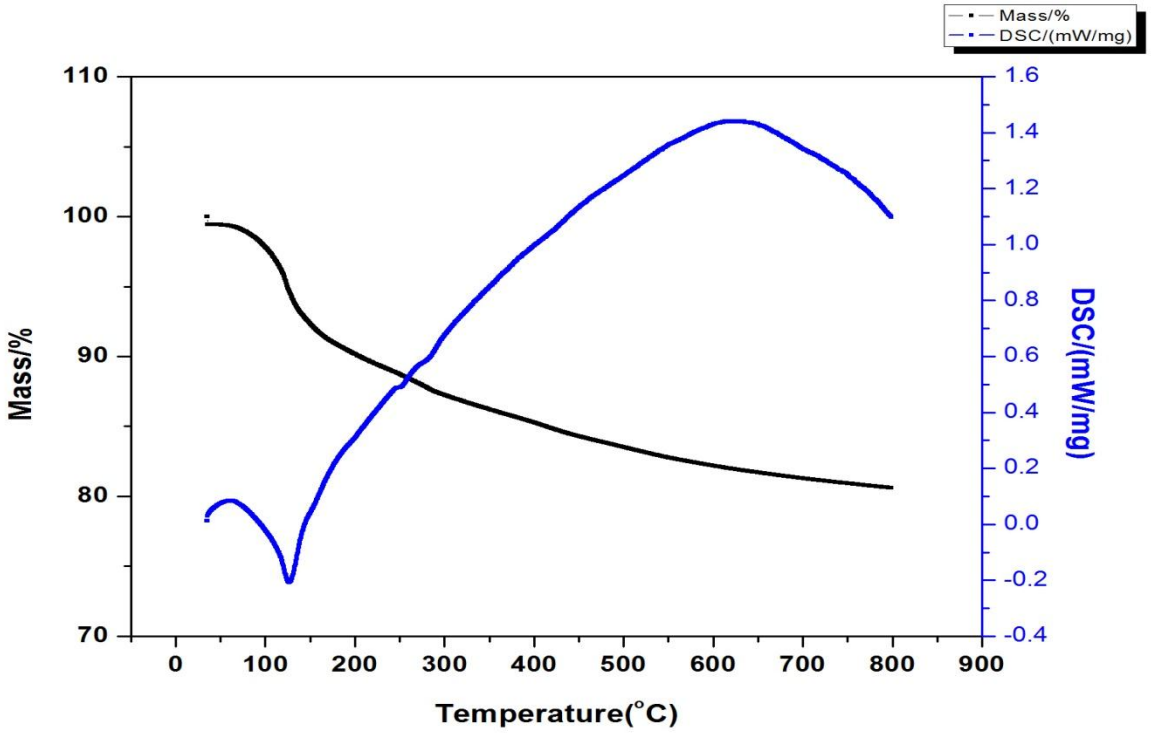


Figure 4.24- DSC and TG of glaze composition – 4 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 16% weight loss. In the first stage the weight loss was 7% due to the removal of the absorbed water and the endothermic peak was shown at 130^{o}C. The second weight loss was around 13%.

4.8.6 DSC AND TG ANALYSIS OF GLAZE COMPOSITION –5

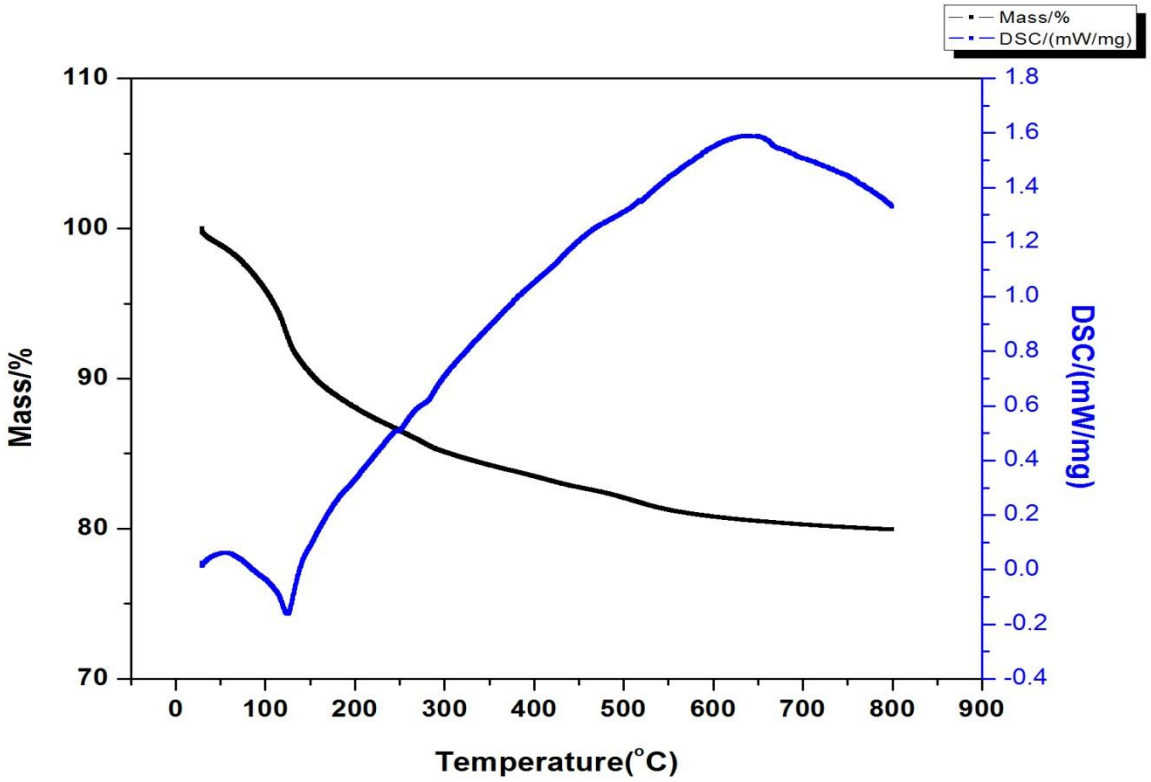


Figure-4.25 DSC and TG of glaze composition – 5 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 17% weight loss. In the first stage the weight loss was 9% due to the removal of the absorbed water and the endothermic peak was shown at 130^{o}C. The second weight loss was around 13%.

4.8.7 DSC AND TG ANALYSIS OF COMPOSITION –6

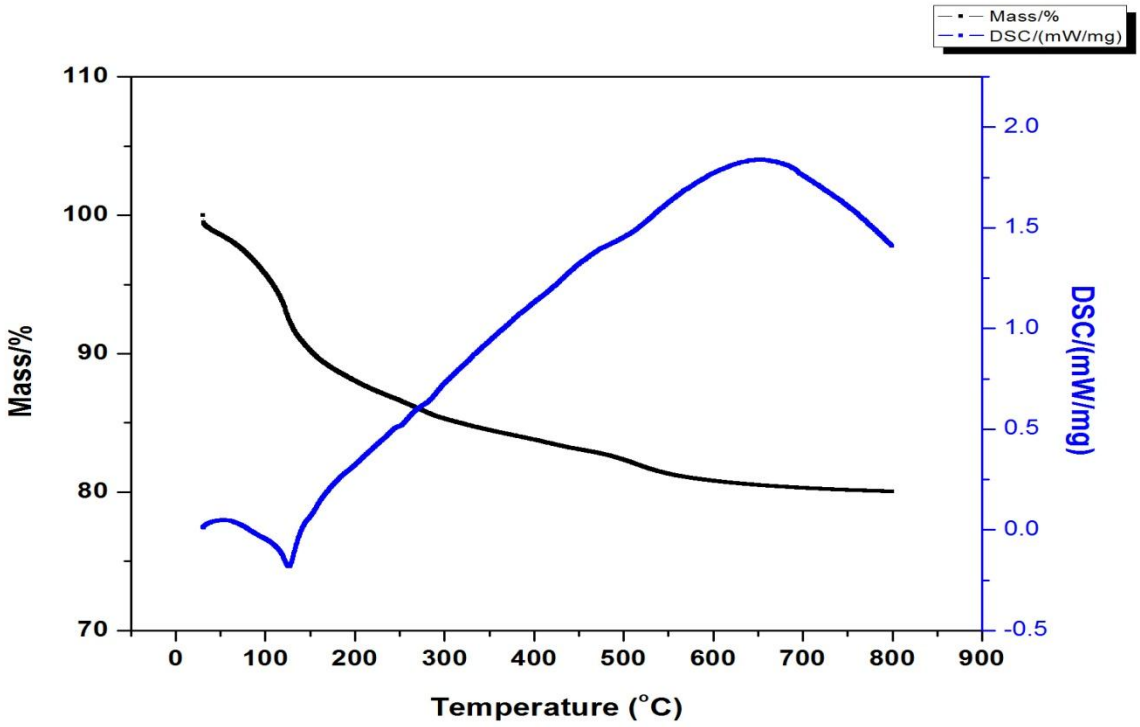


Figure 4.26 DSC and TG of glaze composition – 6 at 800^{o}C

The thermal decomposition of the glass powder was studied by TG-DSC analysis that is shown in the above figure. From the figure it is clearly seen that thermal decomposition of the glass powder was continued till 800^{o}C with 17% weight loss. In the first stage the weight loss was 10% due to the removal of the absorbed water and the endothermic peak was shown at 130^{o}C. The second weight loss was around 10%.

4.8.8 DSC AND TG ANALYSIS OF GLAZE COMPOSITION OF BENTONITE WITH GLASS

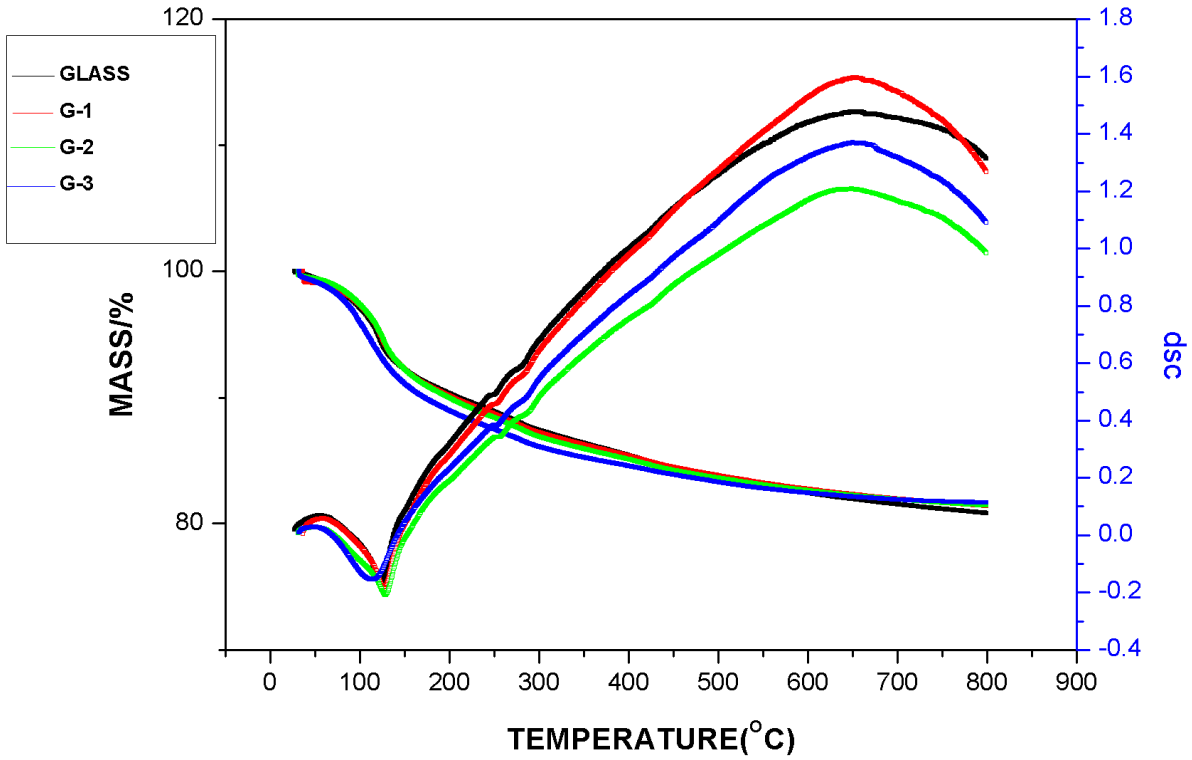


Figure 4.27 DSC and TG of all glaze composition of bentonite with glass

Figure 4.27 shows the simultaneous DSC-TG analysis for four samples *viz bar* samples prepared with glass powders and with a different amount of bentonite (1,5 and 10%). In all the samples an endothermic peak was observed around 125^{o}C. The endothermic peak was associated with a weight loss of above 8- 10% that is attributed to the removal of physically absorbed water. From Tg curve it could be observed that further weight loss of about 10% occurred till 800 ^{o}C for all samples. No appreciable change in weight loss occurred with the addition of bentonite. All the four samples showed broad exothermic peaks in the temperature range 600 ^{o}C to 700 ^{o}C from the DSC curve of figure 4.27 it was observed that there was increase in exothermicity with increase in percentage amount of bentonite.

4.8.9 DSC AND TG ANALYSIS OF GLAZE COMPOSITION OF BALL CLAY WITH GLASS

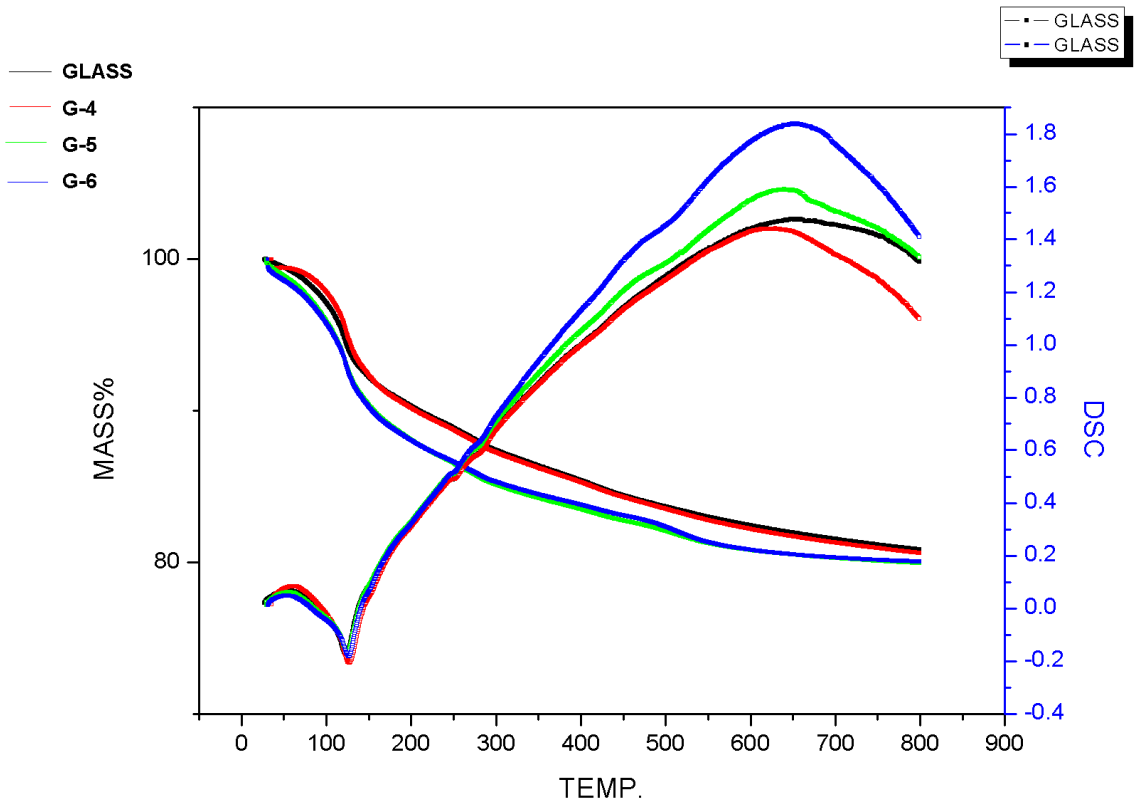


Figure 4.28 DSC and TG analysis of all glaze composition of ball clay with glass

Figure 4.28shows the simultaneous DSC-TG analysis for four samples *viz bar* samples prepared with glass powders and with a different amount of ball clay (1,5 and 10%). In all the samples an endothermic peak was observed around 125^{o}C. The endothermic peak was associated with a weight loss of above 8- 10% that is attributed to the removal of physically absorbed water. From Tg curve it could be observed that further weight loss of about 10% occurred till 800 ^{o}C for all samples. No appreciable change in weight loss occurred with the addition of ball clay. All the four samples showed broad exothermic peaks in the temperature range 600 ^{o}C to 700 ^{o}C from the DSC curve of figure 4.28 it was observed that there was increase in exothermicity with increase in percentage amount of ball clay.

4.9 FTIR ANALYSIS OF GLASS POWDER

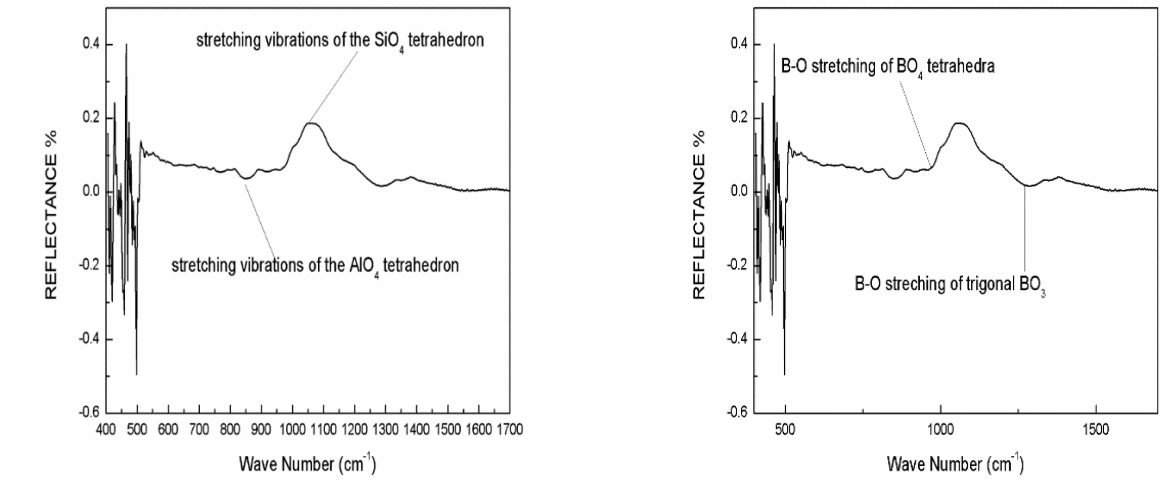


Figure 4.29 FTIR analysis of glass powder

It has been observed from the FTIR analysis graph that is containing tetrahedral SiO_4 and AlO_4 tetrahedral. There is also a little amount of B-O bond is present. Now SiO_4, AlO_4 and BO_4 represent the higher amount of bridging oxygen. Due to AlO_4 tetrahedral presence in glass sample the viscosity is very high and glass having less tendency to crystallization there it can be said that high viscosity value at high temperature are due to presence of SiO_4 and AlO_4 tetrahedral . The peaks are presented between 400 and 600 cm^{-1}which represents Si-O-Al bond that also contribute to the high viscosity.

4.10 **VICKERS HARDNESS OF GLAZED BODY**

The Vickers hardness test was conducted for all the glazed body. At 0.5kgf with 2s dwelling time the Vickers hardness for all glazed samples were calculated and the Vickers hardness value in Hv for all glazed samples were obtained which are as following:

Glazed Body of Glaze Composition – 1 = 503

Glazed Body of Glaze Composition – 2 = 519

Glazed Body of Glaze Composition – 3 = 425

Glazed Body of Glaze Composition - 4 = 515

Glazed Body of Glaze Composition – 5 = 531

Glazed Body of Glaze Composition – 6 = 505

From the above values for all glazed samples it was observed that for glaze composition two and five the Vickers hardness value is high.

4.11 THERMAL SHOCK RESISTANCE OF ALL GLAZED SAMPLES

The thermal shock resistance was determined for all glazed samples by firing at 180^{o}C temperature and then immediately all glazed samples were gone for water bath for 10 minutes. The same procedure was followed for 10 cycles and then a visible inspections for all glazed samples were done to confirm there is a crack or not. Finally it was observed that after completing the 10 cycles of thermal shock test for all glazed samples there was no cracks on the surfaces of the glazed bodies which is the good for glazed body that represents the glazed body has high thermal shock resistance. And high thermal shock resistance that is desired property for the glazed body for tile application. Following figures are showing glazed bodies having no cracks.

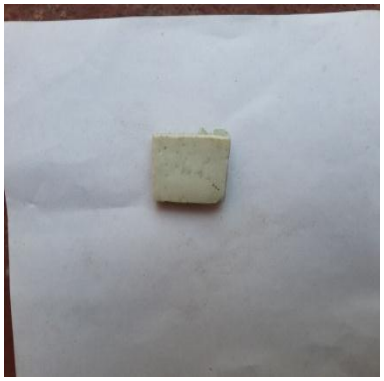
(a)

(b)

(c)

(d)

(e)



(f)

Figure 4.30 glazed samples after thermal shock (a) glazed sample – 4 (b) glazed sample - 3 (c) glazed sample -5 (d) glazed body composition-1 (e) glazed sample -3 (f) glazed sample -6

From the figure it is illustrate that at temperature 150^{o} C firing had been done for all glazed samples and then immediately all glazed samples sent for water bath and repeating this procedure for 10 cycles no cracks were identified which represent high thermal shock resistance for glazed samples.

4.12 CRAZING TEST FOR GLAZED SAMPLES

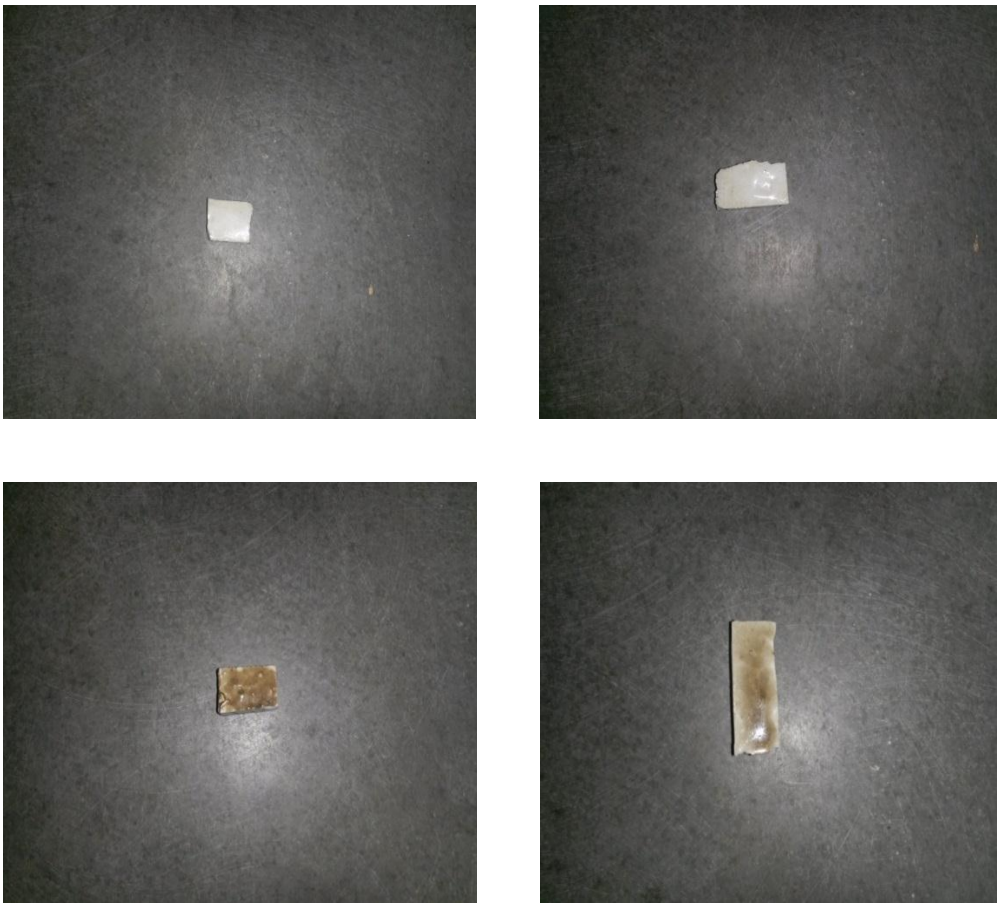


Figure 4.31 glazed samples after crazing test

In autoclave machine at temperature 168^{o}C pressure reached up to 200 kpa and soaking time was given for all glazed samples was one hour and it was done for one cycle only. In one cycle and it was observed after this procedure glazed samples were cleaned with cloth for inspection of the

glaze surface to confirm there is crack or not but it was observed that no cracks were there glazed samples. From the above figure 4.31 it is clearly visualized that after giving the pressure to glazed samples which is 200 kpa at temperature 168^{o}C no cracks or defects were noted which shows or represents that all glazed samples have high crazing resistance and this result of all glazed bodies are welcomed for tile applications

CHAPTER-V

CONCLUSIONS AND REFERENCES

CONCLUSIONS

- Alkali free glaze had been prepared successfully from the alkali-free glass system.
- It had been observed from the dilatometry analysis for glaze compositions of bentonite that increase in percentage amount of bentonite in glaze compositions there is decrease in shrinkage and even for ball clay it was observed by dilatometry analysis that increase in percentage amount of ball clay in glass composition there was decrease in shrinkage.
- It had been observed by comparison of the dilatometry analysis for a various percentage of both ball clay and bentonite with glass composition that the ball clay showed lesser shrinkage than bentonite.
- By flow analysis of the glaze powder of all compositions at different temperatures the flow of the glaze powder starts at $1400^{o}C$ mostly for all six glaze compositions.
- From FTIR analysis it shows there is the presence of AlO_4 and SiO_4 and the peak from 400-600 cm^{-1} there is the presence of the Si-O-Al bond. There is a high concentration of BO in tetrahedral therefore can have tendency to crystallize and high viscosity.
- It had been observed from the thermal shock test that was carried for 10 cycles that no defects were on the glazed samples.
- By crazing test for glazed samples it had been observed that no cracks were found on the glazed samples.

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